DOI: 10.1002/chem.200601017

Diastereoselective Synthesis of 2-Aryl-3-vinyl-2,3-dihydrobenzo[*b*]furans through a Sakurai Reaction: A Mechanistic Proposal

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Abstract: The condensation of 2,3-dihydrobenzoxasilepins with aromatic aldehydes in the presence of boron trifluoride to form 2,3-dihydrobenzofurans shows a level of diastereoselection which is a function of the electronic nature of the aldehyde and the polarity of the solvent. The study of the mechanism of the reaction demonstrated that it proceeds through a ring-opened allylfluorosilane, which is stable enough to be isolated and characterized.

Keywords: aldehydes · allylation · diastereoselectivity · heterocycles · silanes

Introduction

The condensation of allylsilanes with carbonyl compounds under Lewis acid conditions, known as the Sakurai–Hosomi reaction, has been applied successfully in organic synthesis for the formation of C–C bonds.[1,2] In addition, allylsilanes are excellent reagents for the construction of carbocyclic and heterocyclic compounds.[3,4] The 2,3-dihydrobenzofuran ring is the core of the skeleton of an important number of biologically active natural products, such as pterocarpans,[5,6] neolignans,[7,8] as well as synthetic drugs used in the treatment of pulmonary hypertension and atherosclerotic peripheral arterial disease[9] or with protective effects against central nervous system trauma and ischemia.[10] Therefore, much interest has been paid to the development of methods for the stereoselective synthesis of these compounds, mainly Lewis acid promoted reactions,[11,12] anionic cyclizations,[13–15] radical reactions,[16–19] palladium-mediated couplings[20,21] and rhodium catalyzed C–H insertions.[22,23]

In a previous communication, we have reported a novel, two-component methodology, which allows the synthesis of diastereomerically pure dihydrobenzofurans in an easy way.[24] A similar procedure, used for the preparation of trisubstituted tetrahydrofurans, was previously described, independently, by Marsden[25] and Cossy.[26] Our procedure involves the formation of benzoxasilepins by ring-closing metathesis (RCM) followed by a Sakurai–Hosomi-modified reaction. We have described the application of this procedure to the synthesis of pterocarpans[24] and neolignans,[27] although strong differences in the levels of diastereoselectivity were obtained. Other studies have shown that the diastereoselectivity of this procedure is dependent on the reagent.[28–30] Here we present new results which demonstrate the dependence of the diastereoselectivity obtained on the electronic density of the aldehyde, therefore enabling us to control the exclusive formation of *cis* or *trans* diastereomers by adequate selection of the substituents on the aromatic ring.

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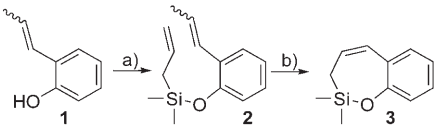
Results and Discussion

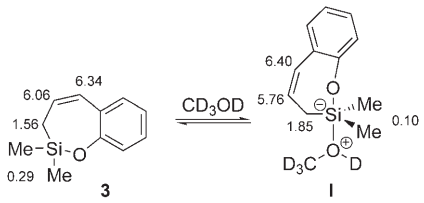
Benzoxasilepins: The 2,3-dihidrobenzo[*f*]oxasilepins required for this study were prepared by RCM of allylsilylethers of *ortho*-allylphenols (Scheme 1). To our knowledge, the behaviour in solution of seven-membered cyclic allylsiloxanes has never been reported, although their synthesis has



Scheme 1. a) Et_3N, $AllylSi(Me)_2Cl$, 0 °C, 4 h, dichloromethane; 90 %; b) Grubbs 2nd generation catalyst, dichloromethane, 30 min, reflux, 91 %.

been described in a variety of ways, including radical cyclizations,[31] titanocene(II)-promoted cyclizations,[32] rhodium mediated C–H insertion[33] and ring-closing metathesis.[34–36]

The NMR spectra of 2,3-dihydrobenzo[*f*]oxasilepin **3** measured in $CDCl_3$ were in agreement with the proposed structure, but when the ^{1}H NMR spectrum was measured in CD_3OD at room temperature, two sets of signals were observed. This can be understood by considering an equilibrium with a zwitterionic, pentacoordinated silicon species (**I**), resulting from the nucleophilic addition of the solvent (Scheme 2).

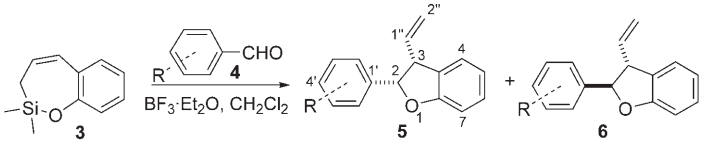


Scheme 2. Behaviour of 2,3-dihydrobenzo[*f*]oxasilepin **3** in CD_3OD.

It is commonly accepted that in pentacoordinated silicon compounds, the most polar atoms prefer the apical positions of a trigonal-bipyramidal arrangement,[37] although these systems usually show some degree of fluxionality.[38] Therefore, we propose structure **I** for this adduct, which is in agreement with the observed spectroscopic properties. Thus, the methyl signals suffer a slight shielding when changing from **3** to the pentacoordinated species **I** (from $\delta = 0.29$ to 0.10 ppm), but only one singlet is observed for both of them in each substance. The CH_2 is somewhat deshielded (from $\delta = 1.56$ to 1.85 ppm) and the double-bond protons also show slight changes in chemical shift and almost the same multiplicity pattern. The relative ratio of these two species, as deduced from the integrals of the ^{1}H NMR spectroscopic signals, is approximately 4:1 for which **3** is the major one. Variable temperature NMR experiments of this solution enabled the construction of a Van't Hoff plot. The calculated thermodynamic constants of the system ($\Delta H = -4.9\ \mathrm{kJ\,mol^{-1}}$ and $\Delta S = -29\ \mathrm{J\,mol^{-1}\,K^{-1}}$) agree with an enthalpically favoured and entropically disfavoured process. Evaporation of the methanol affords quantitatively pure **3**.

In the same way, when the NMR spectrum was measured in non-nucleophilic solvents, such as [D_3]acetonitrile, [D_6]acetone, [D_7]DMF or [D_6]bencene, no splitting of the signals was observed, but in ethanol,[39] again two sets appeared.

Diastereoselectivity of the Sakurai reaction as a function of the nature of the aldehyde: The modified Sakurai–Hosomi condensation of allylsiloxanes with aldehydes has been reported with high levels of diastereoselectivity by Marsden.[28] In our previous papers, we have observed that when the reaction is applied to benzo-fused cyclic allylsiloxanes, complete diastereoselection[24] or a 1:1 mixture is obtained.[27] More extensive experimentation was obviously needed to achieve a better understanding of the factors that control the diastereoselectivity. Thus, we decided to study the influence of the nature of the aldehyde on the stereochemical outcome of the reaction. The benzoxasilepin **3** (without substituents) was used as a substrate, together with a range of substituted benzaldehydes **4** (Scheme 3). All experiments



Scheme 3. Condensation of benzoxasilepin **3** with substituted aldehydes **4**.

were carried out under the same reaction conditions by using $BF_3{\cdot}Et_2O$ as a Lewis acid (2 equiv) and a slight excess of aldehyde (1.1 equiv) referred to benzoxasilepin **3** (Table 1).

The relative stereochemistry of both diastereomers was assigned from their NMR spectroscopic properties. Specially relevant is the shielding of the signal of H-3 in the *trans* isomers **6** when compared to the *cis* isomers **5**. This behaviour can be explained in terms of the influence on this hydrogen of the anisotropy cone of the aromatic ring, as it has been previously observed.[27,28] Appropriate crystals for X-ray diffraction were prepared from **5l** (Figure 1) and **6b** (Figure 2), thus unambiguously establishing the relative stereochemistry for these compounds and for all the **5**/**6** pairs.

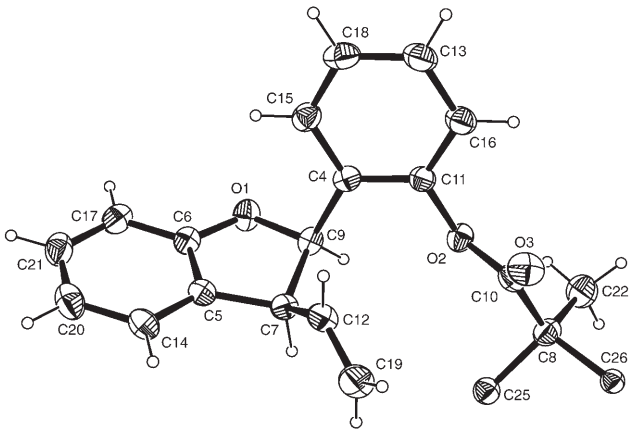
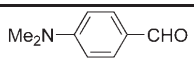
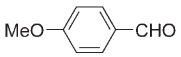
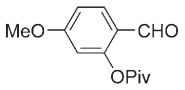
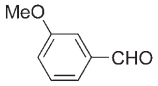
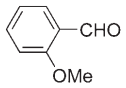
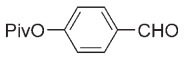
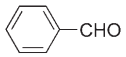
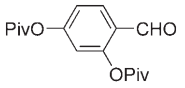
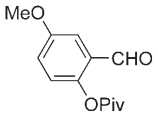
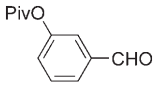
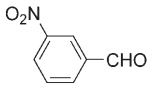
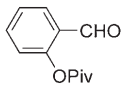
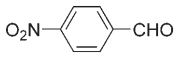


Figure 1. Crystal structure of *cis*-2-(2-pivaloyloxyphenyl)-3-vinyl-2,3-dihydrobenzofuran **5l** (ORTEP 20%).[40]

Although a Hammett plot could not be successfully constructed, it is interesting to note that there is a surprisingly good correlation between the value of δ_H (ArC*H*O) in ^{1}H NMR spectra and the measured *cis*/*trans* ratio. Thus, there is an absolute lack of diastereoselectivity when $\delta_H = 10.0$ ppm (Table 1, entry 7); moving towards higher δ_H values, the major isomer formed has a *cis* relative stereochemistry (**5**). On the other hand, when the value is lower than $\delta = 10.0$ ppm, the major isomer has *trans* relative ster-

Table 1. Synthesis of isomers *cis*/*trans* (**5**/**6**) from **3** and **4**.[a]

Entry	Aldehyde[b]		δ (C*H*O) [ppm]	*cis*/*trans*[c]
1		**4a**	9.72	0:100 (**6a**)
2		**4b**	9.80	0:100 (**6b**)
3		**4c**	9.95	17:83 (**5c**/**6c**)
4		**4d**	9.95	20:80 (**5d**/**6d**)
5		**4e**	10.45[d]	20:80 (**5e**/**6e**)
6		**4f**	9.97	33:67 (**5f**/**6f**)
7		**4g**	10.00	50:50 (**5g**/**6g**)
8		**4h**	10.07	75:25 (**5h**/**6h**)
9		**4i**	10.11	83:17 (**5i**/**6i**)
10		**4j**	10.01	100:0 (**5j**)
11		**4k**	10.11	100:0 (**5k**)
12		**4l**	10.14	100:0 (**5l**)
13		**4m**	10.20	100:0 (**5m**)

[a] In refluxing CH_2Cl_2 overnight; entries are sorted according to increasing ratios of the *cis* isomer **5**. [b] For the synthesis of the noncommercial aldehydes see the Supporting Information. [c] Ratio of isomers determined by ^{1}H NMR spectroscopic analysis of the reaction mixture and confirmed after isolation of the compounds by column chromatography. [d] δ_H value is higher than expected due to intermolecular hydrogen bonding.[42]

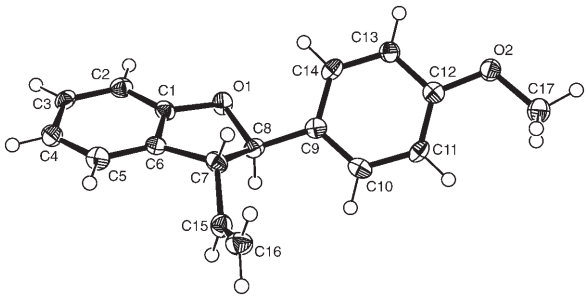


Figure 2. Crystal structure of *trans*-2-(4-methoxyphenyl)-3-vinyl-2,3-dihydrobenzofuran **6b** (ORTEP 50%).[41]

eochemistry (**6**). This correlation has been represented in Figure 3 and it can be a useful tool to know what kind of aldehyde we can choose in order to obtain the *cis* or the *trans* isomer, or what diastereoselection would be obtained for a given substitution pattern. This correlation shows that the potentially more reactive aldehydes, those with higher electrodeficiency and therefore higher δ_H values, offer a greater ratio of *cis* isomer. On the other hand, strong electron-donating groups, such as MeO or Me_2N, lead preferentially to the formation of *trans* isomers.

All the aldehydes presented in Table 1 have oxygenated or nitrogenated substituents. Halogenated substituents were also assayed, and as in other kinds of reactions, their behaviour is somewhat peculiar. Table 2 summarizes the results. *meta*-Substituted aldehydes (entries 2 and 5) lead to the exclusive formation of the *cis* isomers **5**, while *ortho*- and *para*-substituted benzaldehydes (entries 1, 3, 4, and 6) following a common trend, gave rise to *cis*/*trans* mixtures in which the *cis* isomers predominate. These results can be explained on the basis of the two electronic effects of the halogens: when they are in the *ortho* and *para* positions, the opposing effects, electron donation by conjugation and electron withdrawal by induction, make the aldehydes less reac-

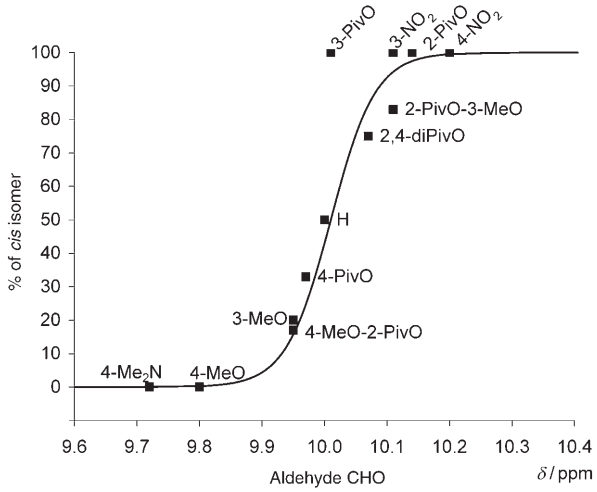
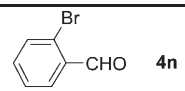
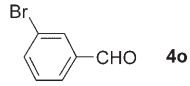
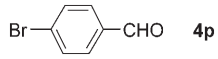
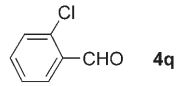
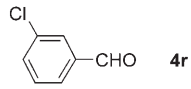
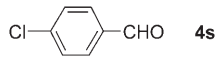


Figure 3. Depiction of the ratio *cis*/*trans* towards the ^{1}H NMR chemical shift of the aldehyde hydrogen in the Sakurai condensation of 2,3-dihydro-2,2-dimethylbenzo[*f*][1,2]oxasilepin (**3**) with aromatic aldehydes.

Table 2. The *cis*/*trans* ratio with halogen-substituted benzaldehydes.[a]

Entry	Aldehyde	*cis*:*trans*[b]
1	 **4n**	72:28 (**5n**/**6n**)
2	 **4o**	100:0 (**5o**)
3	 **4p**	72:28 (**5p**/**6p**)
4	 **4q**	71:29 (**5q**/**6q**)
5	 **4r**	100:0 (**5r**/**6r**)
6	 **4s**	70:30 (**5s**/**6s**)

[a] Isomers *cis*/*trans* (**5**/**6**) prepared from **3** and the appropriate halogenated aldehyde by using 2 equiv of $BF_3{\cdot}Et_2O$ in refluxing CH_2Cl_2. [b] Ratio of isomers determined by ^1H NMR analysis of the reaction mixture and confirmed after isolation of the compounds by column chromatography.

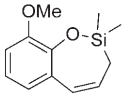
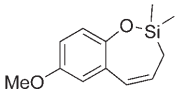
tive than their *meta* isomers, which have only the inductive effect. For each position, chloro or bromo derivatives gave rise to almost identical results.

We have previously described the synthesis of other benzoxasilepins which incorporate methoxyl substituents on the aromatic ring (**7** and **8**).[43] It would be interesting to know if the tendency for diastereomeric behaviour to be affected by the electronic nature of the aldehyde is extensible to those substrates. Thus, **7** and **8** were condensed with some of the previously used aldehydes under the same experimental conditions. The results are listed in Table 3. Again, higher ratios of *cis* isomers were obtained with the more electrodeficient aldehydes.

The influence of the nature of the solvent on the diastereoselectivity of the reaction can be analyzed from the data in Table 4.

As a general trend, an increase in the polarity of the solvent (changing from dichloromethane to CD_3CN) leads to

Table 3. The *cis*/*trans* **5**/**6** ratio starting from different benzoxasilepins.

Entry	Benzoxasilepin	Aldehyde (δ *CHO* [ppm])	*cis*:*trans*[a]
1	 **7**	**4c** (9.95)	9:91 (**5t**/**6t**)
2	**7**	**4h** (10.07) **4c** (9.95)	50:50 (**5u**/**6u**)
3	 **8**		20:80 (**5v**/**6v**)
4	**8**	**4h** (10.07)	91:9 (**5w**/**6w**)
5	**8**	**4i** (10.11)	100:0 (**5x**/**6x**)

[a] Ratio of isomers determined by ^1H NMR spectroscopic analysis of the reaction mixture and confirmed after isolation of the compounds by column chromatography.

Table 4. Influence of the solvent on the ratio of diastereomers.

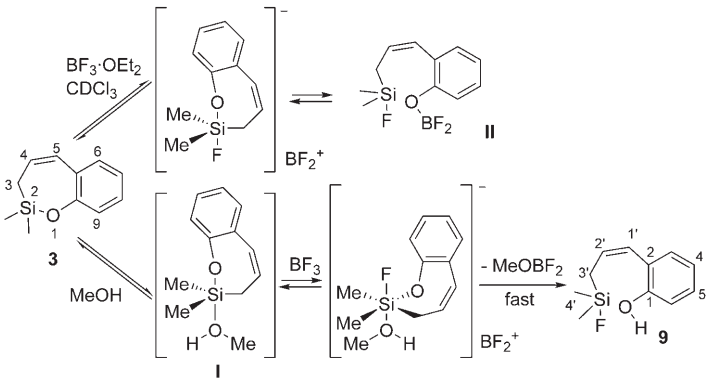
Entry	Substrates	Products	*cis*/*trans*		
			Dichloromethane[a]	CD_3CN[b]	$CDCl_3$[b]
1	**3**+**4a**	**5a**/**6a**	0:100	0:100	–[c]
2	**3**+**4b**	**5b**/**6b**	0:100	20:80	56:44
3	**3**+**4d**	**5d**/**6d**	20:80	62:38	71:29
4	**3**+**4g**	**5g**/**6g**	50:50	63:37	100:0
5	**3**+**4s**	**5s**/**6s**	70:30	77:23	83:17

[a] Conditions from Table 1. [b] Reaction run in a NMR tube at 40 °C in the presence of 2 equiv of $BF_3{\cdot}Et_2O$. [c] The aldehyde precipitates upon addition of the other components.

higher *cis*/*trans* ratios. A particularly strong effect is observed for $CDCl_3$. The higher values for the *cis* isomers in chloroform could arise from a C–H···O hydrogen bond between chloroform and the carbonyl oxygen, which would render the carbonyl group more electron-deficient, as has been previously described for other types of reactions.[44] It is especially interesting to note that an adequate choice of solvent could result in a strong change of diastereoselectivity (entry 4).

Mechanism: Although several mechanisms for this kind of reaction have been proposed,[25,26,28] they do not provide a satisfactory explanation for our results, with regards to the different diastereoselectivity levels as a function of the aldehyde substitution or the solvent polarity.

Thus, we decided to follow the reaction through NMR spectroscopic analysis to detect any possible intermediate which could help to clarify the mechanism. Thus, when two equivalents of $BF_3{\cdot}Et_2O$ were added to a $CDCl_3$ solution of benzoxasilepin **3** and the mixture was monitored by ^1H NMR spectroscopy, the immediate appearance of a new species **II** was observed (Scheme 4). Its relative ratio to-



Scheme 4. Ring opening of **3** leading to **9**.

wards **3** (approximately **II**/**3** 3:7) remains constant for very long periods of time or when more Lewis acid is added. However, when $BF_3{\cdot}Et_2O$ was added to a solution of benzoxasilepin **3** in CD_3OD, the new species **II** was formed instantly and quantitatively. The reaction mixture was worked up, thus enabling the isolation of the fluorinated compound **9**. Its HRMS agreed with a molecular formula $C_{11}H_{15}FOSi$,

which contains one fluorine and hydrogen atom more than the initial heterocycle. The ^{1}H NMR spectrum is very similar to that of the starting material, but for the methyl groups on silicon, which appear as doublets due to their coupling with the ^{19}F (^{3}J(H,F) = 7.4 Hz). This coupling is also observed for the methylene on silicon H3′, which exhibits now an additional splitting (^{3}J(H,F) = 5.8 Hz). Geometry of the double bond can still be established as *Z*. The presence of the fluorine on the silicon is also revealed by the signals for the methyl carbons in the ^{13}C NMR spectrum, which appear as doublets (^{2}J(C,F) = 13.1, 14.9 Hz, respectively). The ^{19}F NMR spectrum shows only one signal at δ = −160.89 ppm (hept t, ^{3}J(F,H) = 7.4, 5.8 Hz) with satellite bands due to the ^{19}F–^{29}Si coupling (^{2}J(F,Si) = 278.6 Hz). A similar spectroscopic behaviour has been reported for other fluorosilanes.[45]

The existence of pentavalent silicon species is well established, and the possibility that a pentavalent intermediate exists in the nucleophilic substitution of silyl ethers has been proposed.[38] In $CDCl_3$, this species would be just an intermediate which evolves into the ring-opened species **II** (Scheme 4). The position of the equilibrium depends on the temperature, and therefore it can be studied through variations on the temperature of acquisition of the NMR spectra. This phenomenon is better observed in a nonprotic solvent with a high boiling point, such as [D$_7$]DMF. Figure 4 shows

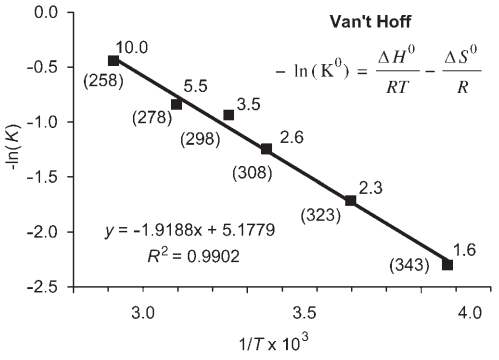


Figure 4. Van't Hoff plot for the equilibrium **3**:**II** in [D$_7$]DMF in the temperature range from 258 to 343 K (values above the line are equilibrium constants *K* in M^{-1}; values in parentheses are temperatures in K).

a Van't Hoff plot for the results when using a large excess of BF_3·Et_2O (>10 equiv), from which the thermodynamic constants of the system can be calculated (ΔH = −15.94 kJ mol^{-1} and ΔS = −43.1 J mol^{-1} K^{-1}). When the temperature is increased, the equilibrium constant drops from 10.0 at 258 K to 1.6 at 343 K. Hence, the reaction with boron trifluoride seems to be an exothermic process which is disfavoured by a decrease in entropy, as it should be for a collision of two molecules into a single one. In other aprotic solvents the behaviour is basically the same. Table 5 depicts the position of the equilibrium at 25 °C, showing that the more polar solvents favour the displacement of the equilibrium towards **II**.

Table 5. Ratio[a] **II**/**3** in different solvents at 25 °C.

Solvent	ε[a]	**3**[b]	**II**[b]
[D$_7$]DMF	36.71	1	3.45
[D$_6$]acetone	20.7	1	0.71
$CDCl_3$	4.807	1	0.64
[D$_6$]benzene	2.274	1	0.50

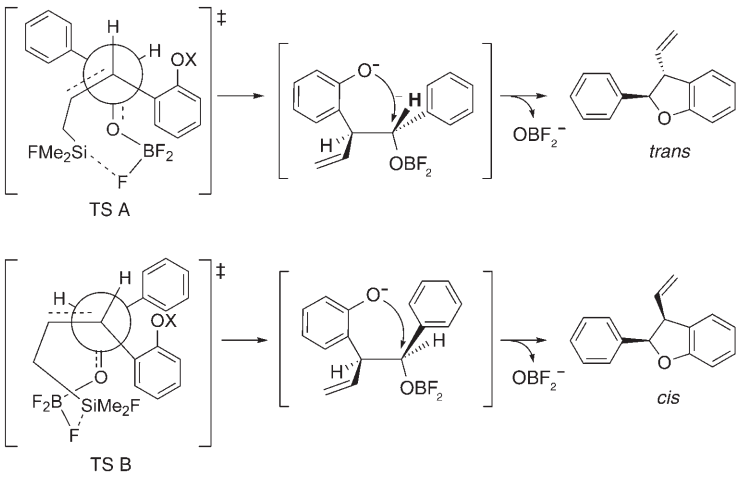
[a] For the corresponding undeuterated solvent, at 25 (±5 °C).[46] [b] Ratio **II**/**3** determined by ^{1}H NMR spectroscopic analysis of the reaction mixture (area of Me_3Si signals).

However, in methanol the process seems to be irreversible, as the only product that can be observed at any temperature is **9** (no signals of **3** could be detected even at −100 °C). In CD_3OD, a solvent attack on the starting material would render the pentavalent silicon species **I**, which would then suffer the attack of the fluoride nucleophile, and eventually, protonation to form **9**.

Although the fluorinated species seemed to be a reaction intermediate, we decided to check whether it was able to react with the aldehydes. Initially, a solution of **9** and benzaldehyde in dichloromethane was refluxed without Lewis acid. No reaction products could be detected after 24 h. But in the presence of one equivalent of BF_3·Et_2O, the reaction smoothly gave the condensation products with the same diastereoselection as when the reaction was performed straight from **3**, such as shown in Tables 1 and 2.

With all these data, we can propose a mechanism for the reaction. It seems clear that the first stage of the reaction is the opening of the benzoxasilepin ring to give a fluorinated species (through a pentacoordinated silicon intermediate) which adds to the carbonyl of the aldehyde, previously activated by the Lewis acid. Two possible diastereomeric transition states, leading to both diastereomers should be written. The dependence of the diastereomeric outcome of the reaction on the polarity of the solvent (Table 4) points to a difference in polarity of those transition states. Bottoni et al. have investigated the mechanism of the Sakurai reaction at the DFT computational level.[47] They found four transition states, quite close in energy, for a model reaction with acetaldehyde, allylsilane and BH_2F, and predicted two of them (each one leading to a different diastereomer) to be associated to the most likely reaction channels in real systems. These are eight-membered cyclic structures, one resembling the boat–boat (BB, TS A) conformation of cyclooctane and the other a type of boat–chair (BC, TS B), in which one of the fluorine atoms from the BF_3 coordinated to the aldehyde approaches the silicon atom, while at the same time the C=C double bond adds to the carbonyl C=O (Scheme 5). Obviously this hypothesis implies the participation of a second BF_3 molecule in the reaction, as we have experimentally observed.

The differences in polarity between the two transition states (TS) could explain the diastereoselectivity of the reaction, the most polar being TS B, as it leads to the *cis* isomers, which are preferred in the more polar solvents. The differences in polarization of the aldehyde C=O double bond due to the effect of the substituents on the aromatic



Scheme 5. Mechanism for the condensation of **II** and **4**.

ring or to the C–H···O hydrogen bond when the solvent is chloroform, should also correspond with significant differences in polarization of the transition states, and hence, in their relative energies.

It is important to note that we have not detected any epimerization processes in these reactions, as has been proposed,[30] and that the reactions performed with other Lewis acids, which differ from BF_3·Et_2O, could proceed through different mechanistic pathways. The main difference between this hypothesis and those previously published for nonbenzofused systems[26,28] is the initial formation of the C–C bond (instead of the C–O bond), a step which controls the stereochemical outcome of the reaction. It should be followed by cyclization through nucleophilic attack on the carbon bearing the OBF_2 group with concomitant inversion of configuration.

Conclusions

In this paper we have advanced the knowledge of the mechanism of a version of the Sakurai reaction, used to prepare natural products with a dihydrobenzofuran skeleton, by the condensation of aromatic aldehydes with benzoxasilepins in the presence of boron trifluoride. We have isolated and identified one of the intermediates of the reaction, a ring-opened allylfluorosilane. The study of the factors that influence the diastereoselection of the reaction shows that the electronic features of the aldehyde and the polarity of the solvent are critical. Two diastereomeric eight-membered cyclic transition states of different polarity can account for the observed stereochemical results.

Experimental Section

General: IR spectra were recorded in liquid film between NaCl plates on a FTIR Mattson Genesis II spectrometer. NMR spectra were determined on a Bruker Avance DPX 300 and Bruker Avance-500 spectrometers. ^{1}H and ^{13}C NMR spectra were recorded in deuterated solvent and are referenced to TMS. Carbon substitution degrees were established by DEPT multipulse sequence, and ^{13}C NMR peak assignments were made with the aid of 2D NMR spectroscopy (HMBC, HMQC, COSY and NOESY). HRMS were registered on an Autospec-Q VG Analytical (FISONS) mass spectrometer. RX data were determined on a Bruker SMART APEX CCD instrument. All solvents were purified and dried following standard procedures.

Allyl[2-(1-propenyl)phenoxy]dimethylsilane (2): Commercially available 2-(1-propenyl)phenol (**1**) (3 g, 22.4 mmol) was dissolved in anhydrous CH_2Cl_2 (110 mL) at 0 °C under a N_2 atmosphere. Anhydrous NEt_3 (3.7 mL, 26.8 mmol) and allylchlorodimethylsilane (3.6 mL, 24.6 mmol) were then added. The reaction mixture was stirred at 0 °C for 4 h, and then a saturated solution of $NaHCO_3/H_2O$ was added. The whole mixture was extracted with CH_2Cl_2. The organic layer was dried over anhydrous Na_2SO_4 and concentrated in vacuo. The residue was purified by flash chromatography, yielding **2** (4.55 g, 20 mmol, 90 %).

*Compound trans-**2** (major isomer)*: Colourless oil; R_f = 0.35 (hexane/Et_2O 98:2); ^{1}H NMR (300 MHz, $CDCl_3$, 25 °C, TMS): δ = 7.46 (dd, ^3J(H,H) = 7.7, ^3J(H,H) = 1.5 Hz, 1H; H-3), 7.13 (td, ^3J(H,H) = 7.7, 1.5 Hz, 1H; H-5), 6.97 (br t, ^3J(H,H) = 7.5 Hz, 1H; H-4), 6.84 (dd, ^3J(H,H) = 8.0, 1.0 Hz, 1H; H-6), 6.71 (dq, ^3J(H,H) = 15.9, 1.6 Hz, 1H; H-1′), 6.22 (dq, ^3J(H,H) = 15.9, 6.6 Hz, 1H; H-2′), 5.85 (ddt, ^3J(H,H) = 16.7, 10.2, 8.2 Hz, 1H; H-2″), 5.02–4.93 (m, 2H; H-3″), 1.93 (dd, ^3J(H,H) = 6.6, 1.7 Hz, 3H; H-3′), 1.82 (d, ^3J(H,H) = 8.1 Hz, 2H; H-1″), 0.30 ppm (s, 6H; $SiMe_2$); ^{13}C NMR (75 MHz, $CDCl_3$, 25 °C, TMS): δ = 151.8 (C, C-1), 133.3 (CH, C-2″), 129.4 (C, C-2), 127.5 (CH, C-5), 126.3 (CH, C-3), 126.1 (CH, C-2′), 125.9 (CH, C-1′), 121.7 (CH, C-4), 119.8 (CH, C-6), 114.3 (CH_2, C-3″), 24.7 (CH_2, C-1″), 18.8 (CH_3, C-3′), −1.7 ppm (CH_3, $SiMe_2$); IR (film): $\tilde{\nu}$ = 2961, 2912, 2881, 2854, 1630, 1596, 1483, 1449, 1253, 1159, 1039, 968, 915, 835 cm^{-1}; HR-EIMS: *m/z*: calcd for $C_{12}H_{21}OSi$: 209.1362 $[M+H]^+$; found: 209.1359.

General procedure for the metathesis of allyl[2-(1-propenyl)phenoxy] dimethylsilanes. Preparation of 2,2-dimethyl-2,3-dihydrobenzo[*f*][1,2]oxasilepins: [1,3-Bis-(2,4,6-trimethylphenyl)-(2-imidazolidinylidene)(dichloro phenylmethylene)(tricyclohexylphosphine)ruthenium] (Grubbs 2nd generation catalyst) was added to a stirred solution of allyl[2-(1-propenyl)phenoxy]dimethylsilanes (0.02 M) in anhydrous CH_2Cl_2 under a N_2 atmosphere. The mixture was stirred under reflux for 30 min, and then the solvent was removed in vacuo. The residue was purified by flash chromatography.

2,2-Dimethyl-2,3-dihydrobenzo[*f*][1,2]oxasilepin (3): Reaction of allyl[2-(1-propenyl)phenoxy]dimethylsilane (**2**) (1.4 g, 6.2 mmol) with Grubbs 2nd generation catalyst (26 mg, 0.03 mmol) in anhydrous CH_2Cl_2 (310 mL) followed by workup, as described in the general procedure, yielded **3** (1.07 g, 5.6 mmol, 91 %). Colourless oil; R_f = 0.34 (hexane/Et_2O 98:2); ^{1}H NMR (300 MHz, $CDCl_3$, 25 °C, TMS): δ = 7.18 (td, ^3J(H,H) = 7.6, 1.3 Hz, 1H; H-7), 7.13 (dd, ^3J(H,H) = 7.7, 1.3 Hz, 1H; H-6), 6.99 (td, ^3J(H,H) = 7.6, 1.3 Hz, 1H; H-8), 6.97 (dd, ^3J(H,H) = 7.6, 1.3 Hz, 1H; H-9), 6.39 (d, ^3J(H,H) = 10.8 Hz, 1H; H-5), 6.10 (dt, ^3J(H,H) = 10.8, 7.5 Hz, 1H; H-4), 1.61 (d, ^3J(H,H) = 7.5 Hz, 2H; H-3), 0.37 ppm (s, 6H; $SiMe_2$); ^{13}C NMR (75 MHz, $CDCl_3$, 25 °C, TMS): δ = 153.2 (C, C-9a), 130.9 (CH, C-6), 128.5 (C, C-5a), 128.1 (CH, C-4), 127.9 (CH, C-7), 126.6 (CH, C-5), 121.4 (CH, C-8*), 121.2 (CH, C-9), 18.2 (CH_2, C-3), −0.5 ppm (CH_3, $SiMe_2$); IR (film): $\tilde{\nu}$ = 3064, 3018, 2958, 2875, 1598, 1565, 1484, 1443 cm^{-1}; HR-EIMS: *m/z*: calcd for $C_{11}H_{15}OSi$: 191.0892 $[M+H]^+$; found: 191.0885; chemical shift and multiplicity of the signals of the mixture **3**+**I**:**3**: ^{1}H NMR (300 MHz, CD_3OD, 25 °C, TMS): δ = 6.34 (d, ^3J(H,H) = 10.8 Hz, 1H), 6.06 (dt, ^3J(H,H) = 10.9, ^3J(H,H) = 7.4 Hz, 1H), 1.56 (d, ^3J(H,H) = 7.4 Hz, 2H), 0.29 ppm (s, 6H); **I**: ^{1}H NMR (300 MHz, CD_3OD, 25 °C, TMS): δ = 6.40 (d, ^3J(H,H) = 11.7 Hz, 1H), 5.76 (dt, ^3J(H,H) = 11.5, ^3J(H,H) = 8.9 Hz, 1H), 1.85 (dd, ^3J(H,H) = 8.8, 1.3 Hz, 2H), 0.10 ppm (s, 6H).

^{1}H NMR spectra of a solution of **3** in CD_3OD were acquired at different temperatures. The ratio **I**/**3** (*K*) was determined by measuring the area of $Si(CH_3)_2$ signals for each compound. *K* (*T* [K]): 0.213 (298), 0.205 (304), 0.193 (313), 0.186 (318), 0.182 (323), 0.178 (328).

2,2-Dimethyl-9-methoxy-2,3-dihydrobenzo[*f*][1,2]oxasilepin (7): Reaction of allyl[2-methoxy-6-(1-propenyl)phenoxy]dimethylsilane (825 mg, 3.16 mmol) with Grubbs 2nd generation catalyst (13 mg, 0.01 mmol) in anhydrous CH_2Cl_2 (150 mL) followed by workup, as described in the general procedure, yielded **7** (650 mg, 2.95 mmol, 93%): White solid; R_f= 0.34 (hexane/Et_2O 98:2); ^{1}H NMR (300 MHz, $CDCl_3$, 25°C, TMS): δ= 6.93 (dd, ^3J(H,H) = 8.1, 7.3 Hz, 1H; H-7), 6.80 (dd, ^3J(H,H) = 8.1, 1.6 Hz, 1H; H-8), 6.73 (dd, ^3J(H,H) = 7.3, 1.6 Hz, 1H; H-6), 6.38 (d, ^3J(H,H) = 10.6 Hz, 1H; H-5), 6.11 (dt, ^3J(H,H) = 10.6, 7.4 Hz, 1H; H-4), 3.87 (s, 3H, OCH_3), 1.58 (d, J = 10.6 Hz, 2H; H-3), 0.38 ppm (s, 6H; $SiMe_2$); ^{13}C NMR (75 MHz, $CDCl_3$, 25°C, TMS): δ = 151.6 (C, C-9), 142.7 (C, C-9a), 129.6 (C, C-5a), 128.5 (CH, C-4), 126.2 (CH, C-5), 122.3 (CH, C-6), 120.9 (CH, C-7), 109.9 (CH, C-8), 55.9 (OCH_3), 18.4 (CH_2, C-3), −0.5 ppm ($SiMe_2$); IR (KBr): $\tilde{\nu}$ = 3014, 2953, 2839, 1572, 1469, 1258, 1079, 918, cm^{-1}; HR-FABMS: m/z: calcd for $C_{12}H_{16}O_2SiNa$ 243.0817 $[M+Na]^+$; found: 243.0820.

2,2-Dimethyl-7-methoxy-2,3-dihydrobenzo[*f*][1,2]oxasilepin (8): Reaction of allyl[4-methoxy-2-(1-propenyl)phenoxy]dimethylsilane (1.48 g, 5.7 mmol) with Grubbs 2nd generation catalyst (24 mg, 0.028 mmol) in anhydrous CH_2Cl_2 (285 mL) followed by workup, as described in the general procedure, yielded **8** (1.13 g, 5.15 mmol, 90%). Colourless oil; R_f= 0.35 (hexane/Et_2O 98:2); ^{1}H NMR (300 MHz, $CDCl_3$, 25°C, TMS): δ= 6.87 (d, ^3J(H,H) = 8.9 Hz, 1H; H-9), 6.73 (dd, ^3J(H,H) = 8.9, 3.1 Hz, 1H; H-8), 6.63 (d, ^3J(H,H) = 3.1 Hz, 1H; H-6), 6.33 (d, ^3J(H,H) = 10.8 Hz, 1H; H-5), 6.09 (dt, ^3J(H,H) = 10.8, 7.4 Hz, 1H; H-4), 3.78 (s, 3H, OCH_3), 1.57 (d, ^3J(H,H) = 7.4 Hz, 2H; H-3), 0.31 ppm (s, 6H; $SiMe_2$); ^{13}C NMR (75 MHz, $CDCl_3$, 25°C, TMS): δ = 153.8 (C, C-7), 147.1 (C, C-9a), 129.0 (C, C-5a), 128.6 (CH, C-4), 126.4 (CH, C-5), 121.8 (CH, C-9), 114.6 (CH, C-6), 113.9 (CH, C-8), 55.6 (OCH_3), 18.2 (CH_2, C-3), −0.7 ppm ($SiMe_2$); IR (film): $\tilde{\nu}$ = 3013, 2950, 2839, 1609, 1490, 1418, 1259, 1220, 1144, 1042, 935, 890, 842, 811 cm^{-1}; HR-EIMS: m/z: calcd for $C_{12}H_{16}O_2Si$: 220.0919 $[M]^+$; found: 220.0919.

General procedure for the Sakurai reaction: BF_3·Et_2O (2 equiv) was added to a stirred solution of the corresponding benzoxasilepin in anhydrous CH_2Cl_2 (4 mL mm^{-1}ol) under a N_2 atmosphere at −45°C. After 5 min, a solution of the aldehyde (1.1 equiv) in CH_2Cl_2 was added dropwise. The reaction mixture was stirred at −45°C for 2 h and was warmed to room temperature. The mixture was then heated to reflux for 4–10 h, diluted with CH_2Cl_2 and washed with brine. The dried (Na_2SO_4) extract was concentrated in vacuo and the *cis*/*trans* ratio was measured by ^{1}H NMR spectroscopy. The major isomers were purified by chromatography over silica gel.

***trans*-2-(4-Dimethylaminophenyl)-3-vinyl-2,3-dihydrobenzofuran (6a)**: Reaction of benzoxasilepin (**3**) (90 mg, 0.47 mmol) with dimethylaminobenzaldehyde (**4a**) (77 mg, 0.52 mmol) and BF_3·Et_2O (120 μL, 0.94 mmol) in anhydrous CH_2Cl_2 (2 mL) followed by workup, as described in the general procedure, yielded **6a** (48%). Colourless oil; R_f = 0.30 (hexane/Et_2O 95:5); ^{1}H NMR (300 MHz, $CDCl_3$, 25°C, TMS): δ = 7.32 (d, ^3J(H,H) = 8.9 Hz, 2H; H-2′, H-6′), 7.21 (dd, ^3J(H,H) = 8.4, 7.3 Hz, 1H; H-6), 7.12 (d, ^3J(H,H) = 7.3 Hz, 1H; H-4), 6.92 (t, ^3J(H,H) = 7.3 Hz, 1H; H-5), 6.87 (d, ^3J(H,H) = 8.4 Hz, 1H; H-7), 6.75 (d, ^3J(H,H) = 8.9 Hz, 2H; H-3′, H-5′), 5.96 (ddd, ^3J(H,H) = 16.9, 9.7, 8.9 Hz, 1H; H-1″), 5.32 (d, ^3J-(H,H) = 8.9 Hz, 1H; H-2), 5.21 (d, ^3J(H,H) = 9.7 Hz, 1H; H-2″a), 5.19 (d, ^3J(H,H) = 16.9 Hz, 1H; H-2″b), 4.01 (dd, ^3J(H,H) = 8.9, 8.5 Hz, 1H; H-3), 2.98 ppm (s, 6H; $N(CH_3)_2$); ^{13}C NMR (75 MHz, $CDCl_3$, 25°C, TMS): δ = 159.3 (C, C-7a), 150.6 (C, C-4′), 137.2 (CH, C-1″), 129.6 (C, C-1′)*, 128.6 (CH, C-6), 128. 0 (C, C-3a)*, 127.3 (CH, C-2′, C-6′), 124.7 (CH, C-4), 1120.5 (CH, C-5), 117.5 (CH_2, C-2″), 112.4 (CH, C-3′, C-5′), 109.5 (CH, C-7), 90.3 (CH, C-2), 55.5 (CH, C-3), 40.5 ppm (CH_3, $N(CH_3)_2$); HREIMS: m/z: calcd for $C_{18}H_{19}NO$: 265.1467 $[M]^+$; found: 265.1464.

***trans*-2-(4-Methoxyphenyl)-3-vinyl-2,3-dihydrobenzofuran (6b)**: Reaction of benzoxasilepin (**3**) (104 mg, 0.55 mmol) with 4-methoxybenzaldehyde (**4b**) (82 mg, 0.60 mmol) and BF_3·Et_2O (140 μL, 1.12 mmol) in anhydrous CH_2Cl_2 (2.5 mL) followed by workup, as described in the general procedure, yielded **6b** (60%). White solid; R_f = 0.28 (hexane/Et_2O 95:5); m.p. 54–56°C; ^{1}H NMR (300 MHz, $CDCl_3$, 25°C, TMS): δ = 7.40 (d, ^3J(H,H) = 8.8 Hz, 2H; H-2′, H-6′), 7.25 (t, ^3J(H,H) = 7.4 Hz, 1H; H-6), 7.14 (br d, ^3J-(H,H) = 7.4 Hz, 1H; H-7), 6.96 (dt, ^3J(H,H) = 7.4, 1.1 Hz, 1H; H-5), 6.95 (d, ^3J(H,H) = 8.8 Hz, 2H; H-3′, H-5′), 6.92 (d, ^3J(H,H) = 7.8 Hz, 1H; H-4), 5.99 (ddd, ^3J(H,H) = 16.9, 10.0, 8.4 Hz, 1H; H-1″), 5.38 (d, ^3J(H,H) = 9.0 Hz, 1H; H-2), 5.26 (ddd, ^3J(H,H) = 10.3, 1.6, 0.5 Hz, 1H; H-2″a), 5.21 (ddd, ^3J(H,H) = 16.9, 1.5, 0.8 Hz, 1H; H-2″b), 4.05 (br dd, ^3J(H,H) = 8.9, 8.4 Hz, 1H; H-3), 3.85 ppm (s, 3H, OCH_3); ^{13}C NMR (75 MHz, $CDCl_3$, 25°C, TMS): δ = 159.5 (C, C-4′), 159.2 (C, C-7a), 137.0 (CH, C-1″), 132.3 (C, C-1′), 129.4 (C, C-3a), 128.7 (CH, C-6), 127.4 (CH, C-2′, C-6′), 124.7 (CH, C-7), 120.8 (CH, C-5), 117.9 (CH_2, C-2″), 114.0 (CH, C-3′, C-5′), 109.6 (CH, C-4), 89.8 (CH, C-2), 56.1 (CH, C-3), 55.3 ppm (CH_3, OCH_3); IR (KBr): $\tilde{\nu}$ = 3070, 2958, 2920, 2835, 1604, 1490, 1469, 1233, 1095, 1029, 969, 801, 750, 668 cm^{-1}; HR-FABMS: m/z: calcd for $C_{17}H_{16}O_2$: 252.1150 $[M]^+$; found: 252.1149.

***cis*-2-(4-Methoxy-2-pivaloyloxyphenyl)-3-vinyl-2,3-dihydrobenzofuran (5c) and *trans*-2-(4-methoxy-2-pivaloyloxyphenyl)-3-vinyl-2,3-dihydrobenzofuran (6c)**: Reaction of benzoxasilepin (**3**) (79 mg, 0.41 mmol) with 4-methoxy-2-pivaloyloxybenzaldehyde (**4c**) (108 mg, 0.45 mmol) and BF_3·Et_2O (104 μL, 0.82 mmol) in anhydrous CH_2Cl_2 (2 mL) followed by workup, as described in the general procedure, yielded **5c**/**6c** 17:83 with an overall yield of 61%.

*Compound **6c***: Colourless oil; R_f = 0.28 (hexane/Et_2O 95:5); ^{1}H NMR (300 MHz, $CDCl_3$, 25°C, TMS): δ = 7.37 (d, ^3J(H,H) = 8.7 Hz 1H; H-6′), 7.21 (t, ^3J(H,H) = 8.0 Hz, 1H; H-6), 7.11 (bd, ^3J(H,H) = 7.2 Hz, 1H; H-4), 6.93 (dt, ^3J(H,H) = 7.4, 0.9 Hz, 1H; H-5), 6.88 (d, ^3J(H,H) = 8.0 Hz, 1H; H-7), 6.80 (dd, ^3J(H,H) = 8.7, 2.5 Hz, 1H; H-5′), 6.59 (d, ^3J(H,H) = 2.5 Hz, 1H; H-3′), 5.92 (ddd, ^3J(H,H) = 17.4, 9.5, 8.3 Hz, 1H; H-1″), 5.48 (d, ^3J(H,H) = 8.3 Hz, 1H; H-2), 5.17 (dd, ^3J(H,H) = 17.4, 9.5 Hz; 2H, H-2″), 4.07 (t, ^3J(H,H) = 8.3 Hz, 1H; H-3), 3.82 (s, 3H; OCH_3), 1.30 ppm (s, 9H, $OCOC(CH_3)_3$); ^{13}C NMR (75 MHz, $CDCl_3$, 25°C, TMS): δ = 176.6 (C, $OCOC(CH_3)_3$), 160.1 (C, C-4′), 159.3 (C, C-7a), 149.5 (C, C-2′), 137.0 (CH, C-1″), 129.0 (C, C-3a), 128.7 (CH, C-6), 128.4 (CH, C-6′), 124.9 (CH, C-4), 124.2 (C, C-1′), 120.9 (CH, C-5), 117.6 (CH_2, C-2″), 112.1 (CH, C-5′), 109.6 (CH, C-7), 108.2 (CH, C-3′), 84.9 (CH, C-2), 55.5 (CH_3, OCH_3), 55.0 (CH, C-3), 39.2 (C, $COC(CH_3)_3$), 27.1 ppm (CH_3, $COC(CH_3)_3$); IR (film): $\tilde{\nu}$ = 3078, 2971, 2932, 2838, 1753, 1618, 1507, 1477, 1460, 1258, 1229, 1155, 974 cm^{-1}; HR-FABMS: m/z: calcd for $C_{22}H_{24}O_4Na$: 375.1572 $[M+Na]^+$; found: 375.1571.

***cis*-2-(3-Methoxyphenyl)-3-vinyl-2,3-dihydrobenzofuran (5d) and *trans*-2-(3-methoxyphenyl)-3-vinyl-2,3-dihydrobenzofuran (6d)**: Reaction of benzoxasilepin (**3**) (70 mg, 0.37 mmol) with 3-methoxybenzaldehyde (**4d**) (55 mg, 0.4 mmol) and BF_3·Et_2O (94 μL, 0.74 mmol) in anhydrous CH_2Cl_2 (2 mL) followed by workup, as described in the general procedure, yielded **5d**/**6d** 20:80 with an overall yield of 62%.

*Compound **5d***: Colourless oil; R_f = 0.30 (hexane/Et_2O 95:5); ^{1}H NMR (300 MHz, $CDCl_3$, 25°C, TMS): δ = 7.24 (m, 1H; H-5′), 7.22 (br d, ^3J-(H,H) = 8.0 Hz, 1H; H-6), 7.15 (br d, ^3J(H,H) = 7.3 Hz, 1H; H-4), 6.95 (m, 2H; H-5, H-7), 6.87 (m, 3H; H-2′, H-4′, H-6′), 5.87 (d, ^3J(H,H) = 9.2 Hz, 1H; H-2), 5.32 (ddd, ^3J(H,H) = 17.0, 9.9, 8.8 Hz, 1H; H-1″), 5.06 (ddd, ^3J(H,H) = 17.0, 1.8, 0.8 Hz, 1H; H-2″b), 4.94 (dd, ^3J(H,H) = 9.9, 1.8 Hz, 1H; H-2″a), 4.31 (br t, ^3J(H,H) = 8.8 Hz, 1H; H-3), 3.81 ppm (s, 3H, OCH_3); ^{13}C NMR (75 MHz, $CDCl_3$, 25°C, TMS): δ = 159.5* (C, C-3′), 159.5* (C, C-7a), 139.5 (C, C-1′), 136.0 (CH, C-1″), 129.2 (CH, C-5′), 129.0 (C, C-3a), 128.7 (CH, C-6), 125.6 (CH, C-4), 120.9 (CH, C-5), 118.8 (CH, C-6′), 116.7 (CH_2, C-2″), 113.0 (CH, C-4′)$^{\#}$, 112.1 (CH, C-2′)$^{\#}$, 109.5 (CH, C-7), 87.1 (CH, C-2), 55.2 (CH_3, OCH_3), 51.6 ppm (CH, C-3); * and $^{\#}$ may be interchanged; HR-EIMS: m/z: calcd for $C_{17}H_{16}O_2$: 252.1150 $[M]^+$; found: 252.1148.

*Compound **6d***: Colourless oil; R_f = 0.29 (hexane/Et_2O 95:5); ^{1}H NMR (300 MHz, $CDCl_3$, 25°C, TMS): δ = 7.31 (t, ^3J(H,H) = 8.0 Hz, 1H; H-5′), 7.22 (t, ^3J(H,H) = 7.6 Hz, 1H; H-6), 7.11 (d, ^3J(H,H) = 7.4 Hz, 1H; H-4), 7.01 (d, ^3J(H,H) = 7.6 Hz, 1H; H-7), 7.00 (1H, br d, H-2′), 6.96 (t, ^3J-(H,H) = 7.4 Hz, 1H; H-5), 6.91 (d, ^3J(H,H) = 8.0 Hz, 1H; H-6′), 6.88 (br d, ^3J(H,H) = 8.0 Hz, 1H; H-4′), 5.99 (ddd, ^3J(H,H) = 17.0, 9.8, 8.5 Hz, 1H; H-1″), 5.39 (d, ^3J(H,H) = 8.9 Hz, 1H; H-2), 5.25 (d, ^3J(H,H) = 9.8 Hz, 1H; H-2″a), 5.21 (d, ^3J(H,H) = 17.0 Hz, 1H; H-2″b), 4.03 (dd, ^3J(H,H) = 8.9, 8.5 Hz, 1H; H-3), 3.83 ppm (s, 3H, OCH_3); ^{13}C NMR (75 MHz, $CDCl_3$, 25°C, TMS): δ = 159.8 (C, C-3′)*, 159.2 (C, C-7a)*, 142.1 (C, C-1′), 137.1 (CH, C-1″), 129.6 (CH, C-5′), 129.1 (C, C-3a), 128.7 (CH, C-6), 124.8 (CH, C-4), 120.9 (CH, C-5), 118.0 (CH, C-6′), 117.9 (CH_2, C-2″),

113.6 (CH, C-4′)[#], 111.2 (CH, C-2′)[#], 109.6 (CH, C-7), 89.6 (CH, C-2), 56.2 (CH, C-3), 55.2 ppm (CH_3, OCH_3); * and [#] may be interchanged; HR-EIMS: *m/z*: calcd for $C_{17}H_{16}O_2$: 252.1150 $[M]^+$; found: 252.1146.

***cis*-2-(2-Methoxyphenyl)-3-vinyl-2,3-dihydrobenzofuran (5e) and *trans*-2-(2-methoxyphenyl)-3-vinyl-2,3-dihydrobenzofuran (6e)**: Reaction of benzoxasilepin (**3**) (102 mg, 0.53 mmol) with 2-methoxybenzaldehyde (**4e**) (80 mg, 0.59 mmol) and $BF_3{\cdot}Et_2O$ (134 μL, 1.06 mmol) in anhydrous CH_2Cl_2 (2.5 mL) followed by workup, as described in the general procedure, yielded **5e**/**6e** 20:80 with an overall yield of 63%.

Compound ***5e***: White solid; R_f=0.27 (hexane/Et_2O 95:5); ^{1}H NMR (300 MHz, $CDCl_3$, 25°C, TMS): δ=7.47 (dd, ^3J(H,H)=7.6, 1.6 Hz, 1H; H-6′), 7.28 (dt, ^3J(H,H)=7.7, 1.6 Hz, 1H; H-4′), 7.21 (ddd, ^3J(H,H)=7.4, 7.2, 0.7 Hz, 1H; H-6), 7.14 (d, ^3J(H,H)=7.2 Hz, 1H; H-4), 6.93 (m, 4H; H-5, H-7, H-3′, H-5′), 6.12 (d, ^3J(H,H)=8.7 Hz, 1H; H-2), 5.30 (ddd, ^3J(H,H)=16.9, 9.8, 8.7 Hz, 1H; H-1″), 4.95 (ddd, ^3J(H,H)=16.9, 1.8, 0.8 Hz, 1H; H-2″b), 4.80 (dd, ^3J(H,H)=9.8, 1.8 Hz, 1H; H-2″a), 4.37 (br dd, ^3J(H,H)=8.9, 8.5 Hz, 1H; H-3), 3.85 ppm (s, 3H; OCH_3); ^{13}C NMR (75 MHz, $CDCl_3$, 25°C, TMS): δ=159.4 (C, C-7a), 155.6 (C, C-2′), 136.5 (CH, C-1″), 129.6 (C, C-3a), 128.4 (CH, C-6), 128.4 (CH, C-4′), 126.9 (C, C-1′), 126.3 (CH, C-6′), 125.7 (CH, C-4), 120.6 (CH, C-5), 120.3 (CH, C-5′), 115.4 (CH_2, C-2″), 109.7 (CH, C-3′), 109.5 (CH, C-7), 83.2 (CH, C-2), 55.1 (CH_3, OCH_3), 50.2 ppm (CH, C-3); IR (KBr): $\tilde{\nu}$=3078, 2962, 2928, 2837, 1604, 1493, 1477, 1461, 1233, 1098, 1029, 969, 801, 750, 668 cm^{-1}; HR-FABMS *m/z*: calcd for $C_{17}H_{16}O_2$: 252.1150 $[M]^+$; found: 252.1151.

Compound ***6e***: Colourless oil; R_f=0.26 (hexane/Et_2O 95:5); ^{1}H NMR (300 MHz, $CDCl_3$, 25°C, TMS): δ=7.43 (dd, ^3J(H,H)=7.6, 1.3 Hz, 1H; H-6′), 7.31 (ddd, ^3J(H,H)=8.0, 7.6, 1.3 Hz, 1H; H-4′), 7.23 (ddd, ^3J(H,H)=7.3, 8.0, 0.7 Hz, 1H; H-6), 7.13 (br d, ^3J(H,H)=7.2 Hz, 1H; H-4), 6.91–7.00 (m, 4H; H-5, H-7, H-3′, H-5′), 6.10 (ddd, ^3J(H,H)=16.8, 10.3, 8.0 Hz, 1H; H-1″), 5.83 (d, ^3J(H,H)=6.7 Hz, 1H; H-2), 5.19–5.12 (m, 2H; H-2″), 4.03 (dd, ^3J(H,H)=8.0, 6.7 Hz, 1H; H-3), 3.86 ppm (s, 3H, OCH_3); ^{13}C NMR (75 MHz, $CDCl_3$, 25°C, TMS): δ=159.5 (C, C-7a), 156.6 (C, C-2′), 138.6 (CH, C-1″), 129.3 (C, C-1′), 129.0 (C, C-3a), 128.9 (CH, C-4′), 128.5 (CH, C-6), 126.4 (CH, C-6′), 125.2 (CH, C-4), 120.6 (CH, C-5), 120.6 (CH, C-5′), 115.8 (CH_2, C-2″), 110.6 (CH, C-3′), 109.5 (CH, C-7), 85.1 (CH, C-2), 55.3 (CH_3, OCH_3), 54.8 ppm (CH, C-3); IR (film): $\tilde{\nu}$=3077, 2934, 2835, 1596, 1477, 1460, 1282, 1244, 1234, 1027, 974, 750 cm^{-1}; HR-FABMS: *m/z*: calcd for $C_{17}H_{16}O_2Na$: 275.1048 $[M+Na]^+$; found: 275.1042.

***cis*-2-(4-Pivaloyloxyphenyl)-3-vinyl-2,3-dihydrobenzofuran (5f) and *trans*-2-(4-pivaloyloxyphenyl)-3-vinyl-2,3-dihydrobenzofuran (6f)**: Reaction of benzoxasilepin (**3**) (110 mg, 0.58 mmol) with 4-pivaloyloxybenzaldehyde (**4f**) (130 mg, 0.63 mmol) and $BF_3{\cdot}Et_2O$ (150 μL, 1.16 mmol) in anhydrous CH_2Cl_2 (3.0 mL) followed by workup, as described in the general procedure, yielded **5f**/**6f** 33:67 with an overall yield of 60%.

Compound ***5f***: White solid; R_f=0.27 (hexane/Et_2O 95:5); ^{1}H NMR (300 MHz, $CDCl_3$, 25°C, TMS): δ=7.29 (d, ^3J(H,H)=8.9 Hz, 2H; H-2′, H-6′), 7.23 (br t, ^3J(H,H)=7.7 Hz, 1H; H-6), 7.13 (br d, ^3J(H,H)=7.3 Hz, 1H; H-4), 7.05 (d, ^3J(H,H)=8.9 Hz, 2H; H-3′, H-5′), 6.95 (dd, ^3J(H,H)=7.7, 0.8 Hz, 1H; H-7), 6.94 (dt, ^3J(H,H)=7.7, 0.8 Hz, 1H; H-5), 5.89 (d, ^3J(H,H)=9.3 Hz, 1H; H-2), 5.29 (ddd, ^3J(H,H)=16.9, 9.7, 8.5 Hz, 1H; H-1″), 5.02 (ddd, ^3J(H,H)=16.9, 2.0, 0.8 Hz, 1H; H-2″b), 4.95 (dd, ^3J(H,H)=9.7, 2.0, Hz, 1H; H-2″a), 4.32 (br t, ^3J(H,H)=8.9 Hz, 1H; H-3), 1.37 ppm (s, 9H, $OCOC(CH_3)_3$); ^{13}C NMR (75 MHz, $CDCl_3$, 25°C, TMS): δ=177.0 (C, $OCOC(CH_3)_3$), 159.4 (C, C-7a), 150.5 (C, C-4′), 136.0 (CH, C-1″),135.2 (C, C-1′), 128.9 (C, C-3a), 128.7 (CH, C-6), 127.4 (CH, C-2′, C-6′), 125.6 (CH, C-4), 121.2 (CH, C-3′, C-5′), 121.0 (CH, C-5), 117.0 (CH_2, C-2″), 109.5 (CH, C-7), 86.7 (CH, C-2), 51.6 (CH, C-3), 39.0 (C, $COC(CH_3)_3$), 27.1 ppm (CH_3, $COC(CH_3)_3$); IR (KBr): $\tilde{\nu}$=3078, 3047, 2974, 1752, 1596, 1476, 1459, 1275, 1228, 1199, 1164, 1116, 1015, 984, 930, 866, 750 cm^{-1}; HR-FABMS: *m/z*: calcd for $C_{21}H_{22}O_3Na$: 345.1467 $[M+Na]^+$; found: 345.1463.

Compound ***6f***: Colourless oil; R_f=0.26 (hexane/Et_2O 95:5); ^{1}H NMR (300 MHz, $CDCl_3$, 25°C, TMS): δ=7.46 (d, ^3J(H,H)=8.7 Hz, 2H; H-2′, H-6′), 7.23 (ddd, ^3J(H,H)=7.9, 7.4, 0.9 Hz, 1H; H-6), 7.12 (br d, ^3J(H,H)=7.4 Hz, 1H; H-4), 7.10 (d, ^3J(H,H)=8.7 Hz, 2H; H-3′, H-5′), 6.95 (dt, ^3J(H,H)=7.4, 0.8 Hz, 1H; H-5), 6.92 (br d, ^3J(H,H)=7.9 Hz, 1H; H-7), 5.99 (ddd, ^3J(H,H)=16.9, 10.1, 8.7 Hz, 1H; H-1″), 5.42 (d, ^3J(H,H)=9.0 Hz, 1H; H-2), 5.27 (dd, ^3J(H,H)=10.1, 1.6 Hz, 1H; H-2″a), 5.21 (ddd, ^3J(H,H)=16.9, 1.6, 0.8 Hz, 1H; H-2″b), 4.02 (br t, ^3J(H,H)=8.9 Hz, 1H; H-3), 1.39 ppm (s, 9H; $OCOC(CH_3)_3$); ^{13}C NMR (75 MHz, $CDCl_3$, 25°C, TMS): δ=177.0 (C, $OCOC(CH_3)_3$), 159.1 (C, C-7a), 150.8 (C, C-4′), 137.8 (C, C-1′), 136.8 (CH, C-1″), 129.1 (C, C-3a), 128.8 (CH, C-6), 126.8 (CH, C-2′, C-6′), 124.8 (CH, C-4), 121.6 (CH, C-3′, C-5′), 121.0 (CH, C-5), 118.1 (CH_2, C-2″), 109.6 (CH, C-7), 89.2 (CH, C-2), 56.3 (CH, C-3), 39.1 (C, $COC(CH_3)_3$), 27.1 ppm (CH_3, $COC(CH_3)_3$); IR (film): $\tilde{\nu}$=3078, 3050, 2974, 2932, 2873, 1750, 1595, 1507, 1477, 1459, 1396, 1365, 1277, 1229, 1199, 1164, 1116, 970, 750 cm^{-1}; HR-FABMS: *m/z*: calcd for $C_{21}H_{22}O_3Na$: 345.1466 $[M+Na]^+$; found: 345.1464.

***cis*-2-Phenyl-3-vinyl-2,3-dihydrobenzofuran (5g) and *trans*-2-phenyl-3-vinyl-2,3-dihydrobenzofuran (6g)**: Reaction of benzoxasilepin (**3**) (85 mg, 0.45 mmol) with benzaldehyde (**4g**) (52 mg, 0.49 mmol) and $BF_3{\cdot}Et_2O$ (114 μL, 0.90 mmol) in anhydrous CH_2Cl_2 (2.5 mL) followed by workup, as described in the general procedure, yielded **5g**/**6g** 50:50 with an overall yield of 58%.

Compound ***5g***: Colourless oil; R_f=0.30 (hexane/Et_2O 95:5); ^{1}H NMR (300 MHz, $CDCl_3$, 25°C, TMS): δ=7.50–7.20 (m, 6H; H-2′, 3′, 4′, 5′, 6′, 6); 7.14 (br d, ^3J(H,H)=7.4 Hz, 1H; H-4); 7.00–6.92 (m, 2H; H-5, 7); 5.91 (d, ^3J(H,H)=9.2 Hz, 1H; H-2); 5.30 (ddd, ^3J(H,H)=17.0, 10.0, 8.8 Hz, 1H; H-1″); 5.04 (dd, ^3J(H,H)=17.0 Hz, 1.9 Hz, 1H; H-2″a); 4.94 (dd, ^3J(H,H)=10.0, 1.9 Hz, 1H; H-2″b), 4.34 ppm (dd, ^3J(H,H)=9.2, 8.8 Hz, 1H; H-3); ^{13}C NMR (75 MHz, $CDCl_3$, 25°C, TMS): δ=159.6 (C, C-7a); 137.9 (C, C-1′); 136.1 (CH, C-1″); 129.0 (C, C-3a); 128.7 (CH, C-6)*; 128.1 (CH, C-3′, C-5′); 127.6 (CH, C-4′)*; 126.4 (CH, C-2′, C-6′); 125.6 (CH, C-4); 120.9 (CH, C-5)[#]; 116.8 (CH_2, C-2″); 109.5 (CH, C-7)[#]; 87.2 (CH, C-2); 51.6 ppm (CH, C-3); * and [#] may be interchanged; IR (film): $\tilde{\nu}$=3065, 3030, 2967, 2924, 1730, 1595, 1470, 1304, 1260, 1227, 1089, 1013, 974, 921, 747, 698 cm^{-1}; HR-EIMS: *m/z*: calcd for $C_{16}H_{15}O$: 223.1123 $[M+H]^+$; found: 223.1121.

Compound ***6g***: Colourless oil; R_f=0.29 (hexane/Et_2O 95:5); ^{1}H NMR (300 MHz, $CDCl_3$, 25°C, TMS): δ=7.47–7.33 (m, 5H; H-2′, H-3′, H-4′, H-5′, H-6′), 7.23 (dd, ^3J(H,H)=7.9, 7.3 Hz, 1H; H-6), 7.12 (d, ^3J(H,H)=7.3 Hz, 1H; H-4), 6.94 (t, ^3J(H,H)=7.3 Hz, 1H; H-5), 6.92 (d, ^3J(H,H)=7.9 Hz, 1H; H-7), 6.00 (ddd, ^3J(H,H)=18.5, 10.2, 8.8 Hz, 1H; H-1″), 5.42 (d, ^3J(H,H)=8.8 Hz, 1H; H-2), 5.25 (br d, ^3J(H,H)=10.2 Hz, 1H; H-2″a), 5.20 (br d, ^3J(H,H)=18.5 Hz, 1H; H-2″b), 4.04 ppm (t, ^3J(H,H)=8.8 Hz, 1H; H-3); ^{13}C NMR (75 MHz, $CDCl_3$, 25°C, TMS): δ=159.2 (C, C-7a), 140.4 (C, C-1′), 137.0 (CH, C-1″), 129.2 (C, C-3a), 128.7 (CH, C-6), 128.5 (CH, C-3′, C-5′), 128.1 (CH, C-4′), 125.8 (CH, C-2′, C-6′), 124.8 (CH, C-4), 120.9 (CH, C-5), 117.9 (CH_2, C-2″), 109.6 (CH, C-7), 89.7 (CH, C-2), 56.2 ppm (CH, C-3); IR (film): $\tilde{\nu}$=3064, 3031, 2959, 2922, 2885, 1638, 1596, 1476, 1262, 1228, 1099, 1014, 982, 922, 865, 750, 697 cm^{-1}; HR-EIMS: *m/z*: calcd for $C_{16}H_{15}O$: 223.1123 $[M+H]^+$; found: 223.1128.

***cis*-2-(2,4-Dipivaloyloxyphenyl)-3-vinyl-2,3-dihydrobenzofuran (5h) and *trans*-2-(2,4-dipivaloyloxyphenyl)-3-vinyl-2,3-dihydrobenzofuran (6h)**: Reaction of benzoxasilepin (**3**) (120 mg, 0.63 mmol) with 2,4-dipivaloyloxybenzaldehyde (**4h**) (212 mg, 0.69 mmol) and $BF_3{\cdot}Et_2O$ (160 μL, 1.26 mmol) in anhydrous CH_2Cl_2 (3.0 mL) followed by workup, as described in the general procedure, yielded **5h**/**6h** 75:25 with an overall yield of 57%.

Compound ***5h***: White solid; R_f=0.29 (hexane/Et_2O 95:5); ^{1}H NMR (300 MHz, $CDCl_3$, 25°C, TMS): δ=7.50 (br d, ^3J(H,H)=7.5 Hz, 1H; H-6′), 7.23 (dt, ^3J(H,H)=7.3, 1.4 Hz, 1H; H-6), 7.14 (br d, ^3J(H,H)=7.2 Hz, 1H; H-4), 6.95 (m, 4H; H-5, H-7, H-3′, H-5′), 5.94 (d, ^3J(H,H)=9.0 Hz, 1H; H-2), 5.33 (ddd, ^3J(H,H)=16.3, 9.8, 8.5 Hz, 1H; H-1″), 4.97 (dd, ^3J(H,H)=16.3, 1.7 Hz, 1H; H-2″b), 4.92 (dd, ^3J(H,H)=9.8, 1.7 Hz, 1H; H-2″a), 4.26 (t, ^3J(H,H)=8.8 Hz, 1H; H-3), 1.40 (s, 9H; $OCOC(CH_3)_3$), 1.36 ppm (s, 9H; $OCOC(CH_3)_3$); ^{13}C NMR (75 MHz, $CDCl_3$, 25°C, TMS): δ=176.6 (C, $COC(CH_3)_3$), 175.8 (C, $OCOC(CH_3)_3$), 159.1 (C, C-7a), 150.6 (C, C-4′), 147.6 (C, C-2′), 135.5 (CH, C-1″), 128.8 (CH, C-6), 128.6 (C, C-3a), 127.5 (CH, C-6′), 127.4 (C, C-1′), 125.8 (CH, C-4), 121.1 (CH, C-5), 118.6 (CH, C-5′), 116.8 (CH_2, C-2″), 115.4 (CH, C-3′), 109.7 (CH, C-7), 82.3 (CH, C-2), 50.6 (CH, C-3), 39.2 (C, $COC(CH_3)_3$), 39.1 (C, $COC(CH_3)_3$), 27.1 (CH_3, $COC(CH_3)_3$), 27.1 ppm (CH_3, $COC(CH_3)_3$); IR (KBr): $\tilde{\nu}$=2974, 2933, 2873, 1755, 1595, 1478, 1460, 1230, 1107, 1028,

978, 901, 751 cm^{-1}; HR-FABMS: *m/z*: calcd for $C_{26}H_{30}O_5Na$: 445.1991 $[M+Na]^+$; found: 445.1990.

***cis*-2-(5-Methoxy-2-pivaloyloxyphenyl)-3-vinyl-2,3-dihydrobenzofuran (5i) and *trans*-2-(5-methoxy-2-pivaloyloxyphenyl)-3-vinyl-2,3-dihydrobenzofuran (6i)**: Reaction of benzoxasilepin (**3**) (112 mg, 0.59 mmol) with 5-methoxy-2-pivaloyloxybenzaldehyde (**4i**) (153 mg, 0.65 mmol) and $BF_3{\cdot}Et_2O$ (150 μL, 1.18 mmol) in anhydrous CH_2Cl_2 (3.0 mL) followed by workup, as described in the general procedure, yielded **5i/6i** 83:17 with an overall yield of 63%.

*Compound **5i***: Colourless oil; R_f=0.30 (hexane/Et_2O 95:5); ^1H NMR (300 MHz, $CDCl_3$, 25°C, TMS): δ=7.23 (dd, ^3J(H,H)=7.7, 7.7 Hz, 1H; H-6), 7.15 (d, ^3J(H,H)=7.3 Hz, 1H; H-4), 7.05 (1H, d, ^3J(H,H)=3.2 Hz; H-6′), 7.01 (d, ^3J(H,H)=8.9 Hz, 1H; H-3′), 6.97 (d, ^3J(H,H)=8.1 Hz, 1H; H-7), 6.95 (dd, ^3J(H,H)=7.7, 7.3 Hz, 1H; H-5), 6.84 (dd, ^3J(H,H)=8.9, 2.8 Hz, 1H; H-4′), 5.90 (d, ^3J(H,H)=8.9 Hz, 1H; H-2), 5.37 (ddd, ^3J(H,H)=17.3, 10.1, 8.5 Hz, 1H; H-1″), 4.96 (br d, ^3J(H,H)=17.3 Hz, 1H; H-2″b), 4.91 (dd, ^3J(H,H)=10.1, 1.6 Hz, 1H; H-2″a), 4.24 (dd, ^3J(H,H)=8.9, 8.5 Hz, 1H; H-3), 3.79 (s, 3H; OCH_3), 1.39 ppm (s, 9H; OCOC-$(CH_3)_3$); ^{13}C NMR (75 MHz, $CDCl_3$, 25°C, TMS): δ=176.5 (C, O*C*OC-$(CH_3)_3$), 159.2 (C, C-7a), 157.0 (C, C-5′), 141.0 (C, C-2′), 135.6 (CH, C-1″), 131.1 (C, C-1′), 128.7 (CH, C-6), 128.7 (C, C-3a), 125.8 (CH, C-4), 122.6 (CH, C-3′), 121.0 (CH, C-5), 116.5 (CH_2, C-2″), 113.7 (CH, C-4′), 112.1 (CH, C-6′), 109.7 (CH, C-7), 82.6 (CH, C-2), 55.6 (CH_3, OCH_3), 50.6 (CH, C-3), 39.1 (C, OCO*C*$(CH_3)_3$), 27.2 ppm (CH_3, OCOC(*C*$H_3)_3$); IR (film): $\tilde{\nu}$=2973, 2934, 2873, 2836, 1751, 1596, 1496, 1478, 1462, 1275, 1232, 1183, 1118, 1040, 980, 752 cm^{-1}; HR-FABMS: *m/z*: calcd for $C_{22}H_{24}O_4Na$ $[M+Na]^+$ 375.1572; found: 375.1573.

***cis*-2-(3-Pivaloyiloxyphenyl)-3-vinyl-2,3-dihydrobenzofuran (5j)**: Reaction of benzoxasilepin (**3**) (66 mg, 0.35 mmol) with *m*-pivaloyloxybenzaldehyde (**4j**) (79 mg, 0.38 mmol) and $BF_3{\cdot}Et_2O$ (88 μL, 0.70 mmol) in anhydrous CH_2Cl_2 (2 mL) followed by workup, as described in the general procedure, yielded **5j** (58%). Colourless oil; R_f=0.28 (hexane/Et_2O 95:5); ^1H NMR (300 MHz, $CDCl_3$, 25°C, TMS): δ=7.36 (t, ^3J(H,H)=7.7 Hz, 1H; H-5′), 7.24 (dt, ^3J(H,H)=7.3, 1.2 Hz, 1H; H-6), 7.14 (d, ^3J-(H,H)=7.7 Hz, 2H; H-4′, H-6′), 7.03–6.92 (m, 4H; H-5, H-7, H-2′, H-4), 5.89 (d, ^3J(H,H)=9.3 Hz, 1H; H-2), 5.32 (ddd, ^3J(H,H)=16.9, 10.1, 9.0 Hz, 1H; H-1″), 5.02 (dd, ^3J(H,H)=16.9, 1.2 Hz, 1H; H-2″b), 4.95 (dd, ^3J(H,H)=10.1, 1.6 Hz, 1H; H-2″a), 4.31 (t, ^3J(H,H)=9.3 Hz, 1H; H-3), 1.37 ppm (s, 9H; OCO$(CH_3)_3$); ^{13}C NMR (75 MHz, $CDCl_3$, 25°C, TMS): δ=176.8 (CO*C*OC$(CH_3)_3$), 159.3 (C, C-7a), 151.1 (C, C-3′), 139.6 (C, C-1′), 135.9 (CH, C-1″), 129.0 (CH, C-5′), 128.9 (C, C-3a), 128.7 (CH, C-6), 125.7 (CH, C-4), 123.6 (CH, C-6′), 121.0 (CH, C-5), 120.6* (CH, C-4′), 119.6* (CH, C-2′), 116.9 (CH_2, C-2″), 109.6 (CH, C-7), 86.6 (CH, C-2), 51.5 (CH, C-3), 39.0 (C, OCO*C*$(CH_3)_3$), 27.1 ppm (CH_3, OCOC(*C*$H_3)_3$); HR-EIMS: *m/z*: calcd for $C_{21}H_{22}O_3$: 322.1569 $[M]^+$; found: 322.1568

***cis*-2-(3-Nitrophenyl)-3-vinyl-2,3-dihydrobenzofuran (5k)**: Reaction of benzoxasilepin (**3**) (69 mg, 0.36 mmol) with *m*-nitrobenzaldehyde (**4k**) (60 mg, 0.40 mmol) and $BF_3{\cdot}Et_2O$ (91 μL, 0.72 mmol) in anhydrous CH_2Cl_2 (2 mL) followed by workup, as described in the general procedure, yielded **5k** (41%). Yellow oil; R_f=0.30 (hexane/Et_2O 95:5); ^1H NMR (300 MHz, $CDCl_3$, 25°C, TMS): δ=8.17 (m, 2H; H-2′, H-4′), 7.64 (d, 1H; ^3J(H,H)=7.7 Hz, H-6′), 7.55 (t, 1H; ^3J(H,H)=7.7 Hz, H-5′), 7.26 (m, 1H; H-6), 7.15 (d, ^3J(H,H)=6.6 Hz, 1H; H-4), 6.99 (m, 2H; H-5, H-7), 5.97 (d, ^3J(H,H)=9.1 Hz, 1H; H-2), 5.21 (ddd, ^3J(H,H)=16.7, 9.5, 9.1 Hz, 1H; H-1″), 5.06 (dd, ^3J(H,H)=16.7, 2.0 Hz, 1H; H-2″b), 4.95 (dd, ^3J(H,H)=9.5, 2.0 Hz, 1H; H-2″a), 4.39 ppm (t, ^3J(H,H)=8.8 Hz, 1H; H-3); ^{13}C NMR (75 MHz, $CDCl_3$, 25°C, TMS): δ=158.2 (C, C-7a), 139.5 (C, C-3′), 135.4 (C, C-1′), 134.7 (CH, C-1″), 131.8* (CH, C-6′), 128.4* (CH, C-5′), 128.3* (CH, C-6), 127.6 (C, C-3a), 124.9 (CH, C-4), 121.9# (CH, C-4′), 120.8# (CH, C-2′), 120.7# (CH, C-5), 117.0 (CH_2, C-2″), 109.0 (CH, C-7), 85.0 (CH, C-2), 50.8 ppm (CH, C-3); * and # may be interchanged; HR-EIMS: *m/z*: calcd for $C_{16}H_{13}NO_3$: 267.0895 $[M]^+$; found: 267.0893.

***cis*-2-(2-Pivaloyloxyphenyl)-3-vinyl-2,3-dihydrobenzofuran (5l)**: Reaction of benzoxasilepin (**3**) (115 mg, 0.6 mmol) with 2-pivaloyloxybenzaldehyde (**4l**) (137 mg, 0.66 mmol) and $BF_3{\cdot}Et_2O$ (150 μL, 1.2 mmol) in anhydrous CH_2Cl_2 (3 mL) followed by workup, as described in the general procedure, yielded **5l** (61%). White solid; R_f=0.28 (hexane/Et_2O 95:5); m.p. 64–66°C; ^1H NMR (300 MHz, $CDCl_3$, 25°C, TMS): δ=7.52 (dd, ^3J(H,H)=7.7, 1.7 Hz, 1H; H-3′), 7.34 (dt, ^3J(H,H)=8.0, 1.7 Hz, 1H; H-5′), 7.24 (m, 2H; H-4′, H-6), 7.15 (d, ^3J(H,H)=7.3 Hz, 1H; H-4), 7.11 (dd, ^3J(H,H)=8.0, 1.1 Hz, 1H; H-6′), 6.98 (br d, ^3J(H,H)=8.1 Hz, 1H; H-7), 6.95 (dt, ^3J(H,H)=7.3, 1.0 Hz, 1H; H-5), 5.98 (d, ^3J(H,H)=8.9 Hz, 1H; H-2), 5.33 (ddd, ^3J(H,H)=17.0, 9.9, 8.9 Hz, 1H; H-1″), 4.98 (dd, ^3J(H,H)=17.0, 1.7 Hz, 1H; H-2″b), 4.90 (dd, ^3J(H,H)=9.9, 1.7 Hz, 1H; H-2″a), 4.28 (t, ^3J(H,H)=8.9 Hz, 1H; H-3), 1.41 ppm (s, 9H; OCOC-$(CH_3)_3$); ^{13}C NMR (75 MHz, $CDCl_3$, 25°C, TMS): δ=176.2 (C, O*C*OC-$(CH_3)_3$), 159.3 (C, C-7a), 147.5 (C, C-2′), 135.7 (CH, C-1″), 130.1 (C, C-1′), 128.8 (CH, C-6), 128.7 (C, C-3a), 128.4 (CH, C-5′), 127.2 (CH, C-3′), 125.8 (CH, C-4), 125.5 (CH, C-4′), 121.7 (CH, C-6′), 121.0 (CH, C-5), 116.6 (CH_2, C-2″), 109.7 (CH, C-7), 82.5 (CH, C-2), 50.6 (CH, C-3), 39.2 (C, CO*C*$(CH_3)_3$), 27.2 ppm (CH_3, COC(*C*$H_3)_3$); IR (KBr): $\tilde{\nu}$=3078, 3047, 2974, 1752, 1596, 1476, 1459, 1275, 1228, 1199, 1164, 1116, 1015, 984, 930, 866, 750 cm^{-1}; HR-FABMS: *m/z*: calcd for $C_{21}H_{22}O_3Na$: 345.1467 $[M+Na]^+$; found: 345.1466.

***cis*-2-(4-Nitrophenyl)-3-vinyl-2,3-dihydrobenzofuran (5m)**: Reaction of benzoxasilepin (**3**) (107 mg, 0.56 mmol) with 4-nitrobenzaldehyde (**4m**) (94 mg, 0.62 mmol) and $BF_3{\cdot}Et_2O$ (140 μL, 1.12 mmol) in anhydrous CH_2Cl_2 (3 mL) followed by workup, as described in the general procedure, yielded **5m** (30%). Yellow oil; R_f=0.29 (hexane/Et_2O 95:5); ^1H NMR (300 MHz, $CDCl_3$, 25°C, TMS): δ=8.23 (d, ^3J(H,H)=8.9 Hz, 2H; H-3′, H-5′), 7.48 (d, ^3J(H,H)=8.9 Hz, 2H; H-2′, H-6′), 7.26 (m, 1H; H-6), 7.14 (d, ^3J(H,H)=7.1 Hz, 1H; H-4), 6.99 (m, 2H; H-5, H-7), 5.97 (d, ^3J(H,H)=9.5 Hz, 1H; H-2), 5.17 (ddd, ^3J(H,H)=16.9, 9.4, 8.8 Hz, 1H; H-1″), 5.06 (dd, ^3J(H,H)=16.9, 2.3 Hz, 1H; H-2″b), 4.95 (dd, ^3J(H,H)=9.4, 2.3, Hz, 1H; H-2″a), 4.40 ppm (dd, ^3J(H,H)=9.5, 8.9 Hz, 1H; H-3); ^{13}C NMR (75 MHz, $CDCl_3$, 25°C, TMS): δ=159.0 (C, C-7a), 147.4 (C, C-4′), 145.4 (C, C-1′), 135.3 (CH, C-1″), 129.1 (CH, C-6), 128.3 (C, C-3a), 127.3 (CH, C-2′, C-6′), 125.7 (CH, C-4), 123.4 (CH, C-3′, C-5′), 121.5 (CH, C-5), 117.7 (CH_2, C-2″), 109.7 (CH, C-7), 86.0 (CH, C-2), 51.7 ppm (CH, C-3); HR-EIMS: *m/z*: calcd for $C_{16}H_{13}NO_3$: 267.0895 $[M]^+$; found: 267.0897.

***cis*-2-(2-Bromophenyl)-3-vinyl-2,3-dihydrobenzofuran (5n) and *trans*-2-(2-bromophenyl)-3-vinyl-2,3-dihydrobenzofuran (6n)**: Reaction of benzoxasilepin (**3**) (107 mg, 0.56 mmol) with *o*-bromobenzaldehyde (**4n**) (65 mg, 0.35 mmol) and $BF_3{\cdot}Et_2O$ (81 μL, 0.64 mmol) in anhydrous CH_2Cl_2 (3 mL) followed by workup, as described in the general procedure, yielded **5n/6n** (72:28) with an overall yield of 58%; R_f=0.27 (hexane/Et_2O 95:5).

*Compound **5n***: Colourless oil; ^1H NMR (300 MHz, $CDCl_3$, 25°C, TMS): δ=7.56 (m, 2H; H-3′, H-5′), 7.36–7.15 (m, 4H; H-4, H-6, H-4′, H-6′), 6.96 (m, 2H; H-5, H-7)), 6.12 (d, 1H; ^3J(H,H)=8.9 Hz, H-2), 5.26 (ddd, ^3J(H,H)=16.9, 9.8, 8.9 Hz, 1H; H-1″), 5.03 (ddd, ^3J(H,H)=16.9, 1.7, 0.8 Hz, 1H; H-2″b), 4.84 (dd, ^3J(H,H)=9.8, 1.7 Hz, 1H; H-2″a), 4.53 ppm (br t, ^3J(H,H)=8.9 Hz, 1H; H-3); ^{13}C NMR (75 MHz, $CDCl_3$, 25°C, TMS): δ=159.1 (C, C-7a), 137.8 (C, C-1′), 135.5 (CH, C-1″), 132.3 (CH, C-3′), 129.0* (CH, C-6′), 128.8 (C, C-3a), 128.7 (CH, C-6), 127.9* (CH, C-5′), 127.2* (CH, C-4′), 125.9 (CH, C-4), 121.5 (C, C-2′), 121.1 (CH, C-5), 116.4 (CH_2, C-2″), 109.6 (CH, C-7), 86.3 (CH, C-2), 49.6 ppm (CH, C-3); * may be interchanged; HR-EIMS: *m/z*: calcd for $C_{16}H_{13}{}^{79}BrO$: 300.0150 $[M]^+$; found: 300.0151.

***cis*-2-(3-Bromophenyl)-3-vinyl-2,3-dihydrobenzofuran (5o)**: Reaction of benzoxasilepin (**3**) (69 mg, 0.36 mmol) with *m*-bromobenzaldehyde (**4o**) (74 mg, 0.40 mmol) and $BF_3{\cdot}Et_2O$ (91 μL, 0.72 mmol) in anhydrous CH_2Cl_2 (2 mL) followed by workup, as described in the general procedure, yielded **5o** (58%). Colourless oil; R_f=0.29 (hexane/Et_2O 95:5); ^1H NMR (300 MHz, $CDCl_3$, 25°C, TMS): δ=7.44 (m, 2H; H-2′, H-4′), 7.21 (m, 3H; H-6, H-5′, H-6′), 7.14 (1H, dd, ^3J(H,H)=7.8, 1.1 Hz; H-4), 6.97 (m, 2H; H-5, H-7), 5.85 (d, ^3J(H,H)=8.9 Hz, 1H; H-2), 5.27 (ddd, ^3J(H,H)=17.0, 9.8, 8.8 Hz, 1H; H-1″), 5.04 (dd, ^3J(H,H)=17.0, 1.9 Hz, 1H; H-2″b), 4.97 (dd, ^3J(H,H)=9.8, 1.9 Hz, 1H; H-2″a), 4.32 ppm (t, ^3J(H,H)=8.9 Hz, 1H; H-3). ^{13}C NMR (75 MHz, $CDCl_3$, 25°C, TMS): δ=159.2 (C, C-7a), 140.3 (C, C-1′), 135.7 (CH, C-1″), 130.7* (CH, C-5′), 129.7* (CH, C-4′), 129.4* (CH, C-2′), 128.8 (CH, C-6), 128.7 (C, C-3a), 125.6 (CH, C-4)#, 125.1 (CH, C-6′)#, 122.4 (C, C-3′), 121.1 (CH, C-5), 117.2 (CH_2, C-2″), 109.6 (CH, C-7), 86.2 (CH, C-2), 51.6 ppm (CH, C-3);

* and # may be interchanged; HR-EIMS: *m/z*: calcd for $C_{16}H_{13}{}^{79}BrO$: 300.0150 $[M]^+$; found: 300.0148.

***cis*-2-(4-Bromophenyl)-3-vinyl-2,3-dihydrobenzofuran (5p) and *trans*-2-(4-bromophenyl)-3-vinyl-2,3-dihydrobenzofuran (6p)**: Reaction of benzoxasilepin (**3**) (84 mg, 0.44 mmol) with *p*-bromobenzaldehyde (**4p**) (90 mg, 0.48 mmol) and $BF_3{\cdot}Et_2O$ (110 μL, 0.88 mmol) in anhydrous CH_2Cl_2 (2 mL) followed by workup, as described in the general procedure, yielded **5p**/**6p** (72:28) with an overall yield of 56%.

*Compound **5p***: Colourless oil; R_f=0.30 (hexane/Et_2O 95:5); ^{1}H NMR (300 MHz, $CDCl_3$, 25°C, TMS): δ=7.48 (d, ^3J(H,H)=8.4 Hz, 2H; H-3′, H-5′), 7.24 (dt, ^3J(H,H)=7.3, 0.8 Hz, 1H; H-6), 7.17 (d, ^3J(H,H)=8.4 Hz, 2H; H-2′, H-6′), 7.13 (br d, ^3J(H,H)=7.7 Hz, 1H; H-4), 6.95 (m, 2H; H-5, H-7), 5.85 (d, ^3J(H,H)=9.3 Hz, 1H; H-2), 5.25 (ddd, ^3J(H,H)=16.9, 9.7, 8.8 Hz, 1H; H-1″), 5.04 (ddd, ^3J(H,H)=16.9, 2.0, 0.8 Hz, 1H; H-2″b), 4.96 (dd, ^3J(H,H)=9.7, 2.0 Hz, 1H; H-2″a), 4.32 ppm (br t, ^3J(H,H)=9.1 Hz, 1H; H-3); ^{13}C NMR (75 MHz, $CDCl_3$, 25°C, TMS): δ=159.3 (C, C-7a), 137.0 (C, C-4′), 135.8 (CH, C-1″), 131.3 (CH, C-3′, C-5′), 128.8 (CH, C-6), 128.7 (C, C-1′), 128.1 (CH, C-2′, C-6′), 125.6 (CH, C-4), 121.5 (C, C-3a), 121.1 (CH, C-5), 117.1 (CH_2, C-2″), 109.5 (CH, C-7), 86.5 (CH, C-2), 51.5 ppm (CH, C-3); HR-EIMS: *m/z*: calcd for $C_{16}H_{13}{}^{79}BrO$: 300.0150 $[M]^+$; found: 300.0146.

***cis*-2-(2-Chlorophenyl)-3-vinyl-2,3-dihydrobenzofuran (5q) and *trans*-2-(2-chlorophenyl)-3-vinyl-2,3-dihydrobenzofuran (6q)**: Reaction of benzoxasilepin (**3**) (74 mg, 0.39 mmol) with *o*-chlorobenzaldehyde (**4q**) (60 mg, 0.42 mmol) and $BF_3{\cdot}Et_2O$ (100 μL, 0.78 mmol) in anhydrous CH_2Cl_2 (2 mL) followed by workup, as described in the general procedure, yielded **5q**/**6q** 71:29 with an overall yield of 59%.

*Compound **5q***: Colourless oil; R_f=0.27 (hexane/Et_2O 95:5); ^{1}H NMR (300 MHz, $CDCl_3$, 25°C, TMS): δ=7.57 (dd, ^3J(H,H)=7.2, 2.2 Hz, 1H; H-3′), 7.38 (dd, ^3J(H,H)=7.6, 2.2 Hz, 1H; H-5′), 7.39–7.21 (m, 3H; H-6, H-4′, H-6′), 7.16 (br d, ^3J(H,H)=7.4 Hz, 1H; H-4), 6.97 (br d, ^3J(H,H)=7.6 Hz, 1H; H-7), 6.95 (dt, ^3J(H,H)=7.4, 1.0 Hz, 1H; H-5), 6.16 (d, ^3J(H,H)=8.8 Hz, 1H; H-2), 5.28 (ddd, ^3J(H,H)=16.9, 9.9, 8.8 Hz, 1H; H-1″), 5.02 (ddd, ^3J(H,H)=16.9, 1.9, 0.8 Hz, 1H; H-2″b), 4.83 (ddd, ^3J(H,H)=9.9, 1.9, 0.5 Hz, 1H; H-2″a), 4.49 ppm (br t, ^3J(H,H)=8.8 Hz, 1H; H-3); ^{13}C NMR (75 MHz, $CDCl_3$, 25°C, TMS): δ=159.1 (C, C-7a), 137.8 (C, C-1′)*, 136.3 (C, C-2′)*, 135.5 (CH, C-1″), 129.0 (CH, C-5′)#, 128.9 (C, C-3a), 128.8 (CH, C-6, C-3′#), 127.4 (CH, C-6′)#, 126.7 (CH, C-4′)#, 125.9 (CH, C-4), 121.1 (CH, C-5), 116.4 (CH_2, C-2″), 109.6 (CH, C-7), 84.5 (CH, C-2), 49.8 ppm (CH, C-3); * and # may be interchanged; HR-EIMS: *m/z*: calcd for $C_{16}H_{13}ClO$: 256.0655 $[M]^+$; found: 256.0654.

***cis*-2-(3-Chlorophenyl)-3-vinyl-2,3-dihydrobenzofuran (5r)**: Reaction of benzoxasilepin (**3**) (78 mg, 0.41 mmol) with *m*-chlorobenzaldehyde (**4r**) (63 mg, 0.45 mmol) and $BF_3{\cdot}Et_2O$ (105 μL, 0.82 mmol) in anhydrous CH_2Cl_2 (2 mL) followed by workup, as described in the general procedure, yielded **5r** (59%). Colourless oil; ^{1}H NMR (300 MHz, $CDCl_3$, 25°C, TMS): δ=7.29 (m, 3H; H-2′, H-4′, H-6′), 7.23 (m, 1H; H-6), 7.18 (m, 1H; H-5′), 7.13 (d, ^3J(H,H)=8.1 Hz, 1H; H-4), 6.95 (m, 2H; H-5, H-7), 5.86 (d, ^3J(H,H)=9.3 Hz, 1H; H-2), 5.28 (ddd, ^3J(H,H)=16.9, 9.7, 9.3 Hz, 1H; H-1″), 5.05 (dd, ^3J(H,H)=16.9, 1.6 Hz, 1H; H-2″b), 4.97 (dd, ^3J(H,H)=9.7, 1.6 Hz, 1H; H-2″a), 4.33 ppm (t, ^3J(H,H)=9.3 Hz, 1H; H-3); ^{13}C NMR (75 MHz, $CDCl_3$, 25°C, TMS): δ=159.2 (C, C-7a), 140.1 (C, C-1′), 135.7 (CH, C-1″), 134.2 (C, C-3′), 129.4 (CH, C-5′), 128.8 (CH, C-6), 128.7 (C, C-3a), 127.8* (CH, C-4′), 126.5* (CH, C-2′), 125.6 (CH, C-4), 124.7 (CH, C-6′), 121.1 (CH, C-5), 117.2 (CH_2, C-2″), 109.6 (CH, C-7), 86.3 (CH, C-2), 51.6 ppm (CH, C-3); * may be interchanged; HR-EIMS: *m/z*: calcd for $C_{16}H_{13}ClO$: 256.0655 $[M]^+$; found: 256.0657.

***cis*-2-(4-Chlorophenyl)-3-vinyl-2,3-dihydrobenzofuran (5s) and *trans*-2-(4-chlorophenyl)-3-vinyl-2,3-dihydrobenzofuran (6s)**: Reaction of benzoxasilepin (**3**) (61 mg, 0.32 mmol) with *p*-chlorobenzaldehyde (**4s**) (49 mg, 0.35 mmol) and $BF_3{\cdot}Et_2O$ (82 μL, 0.64 mmol) in anhydrous CH_2Cl_2 (2 mL) followed by workup, as described in the general procedure, yielded **5s**/**6s** 70:30 with an overall yield of 58%.

*Compound **5s***: Colourless oil; ^{1}H NMR (300 MHz, $CDCl_3$, 25°C, TMS): δ=7.33 (d, ^3J(H,H)=8.5 Hz, 2H; H-3′, H-5′), 7.22 (m, 2H; H-6, H-2′, H-6′), 7.13 (br d, ^3J(H,H)=7.8 Hz, 1H; H-4), 6.95 (m, 2H; H-5, H-7), 5.86 (d, ^3J(H,H)=9.4 Hz, 1H; H-2), 5.26 (ddd, ^3J(H,H)=16.9, 9.7, 9.0 Hz, 1H; H-1″), 5.04 (ddd, ^3J(H,H)=16.9, 1.8, 0.7 Hz, 1H; H-2″b), 4.95 (dd, ^3J(H,H)=9.7, 1.8 Hz, 1H; H-2″a), 4.32 ppm (br t, ^3J(H,H)=9.0 Hz, 1H; H-3); ^{13}C NMR (75 MHz, $CDCl_3$, 25°C, TMS): δ=159.3 (C, C-7a), 136.5 (C, C-1′), 135.8 (CH, C-1″), 133.3 (C, C-4′), 128.8 (CH, C-6), 128.7 (C, C-3a), 128.3 (2CH, C-3′, C-5′), 127.8 (2CH, C-2′, C-6′), 125.6 (CH, C-4), 121.1 (CH, C-5), 117.1 (CH_2, C-2″), 109.5 (CH, C-7), 86.5 (CH, C-2), 51.5 ppm (CH, C-3); HR-EIMS: *m/z*: calcd for $C_{16}H_{13}ClO$: 256.0655 $[M]^+$; found: 256.0653.

***cis*-7-Methoxy-2-(4-methoxy-2-pivaloyloxyphenyl)-3-vinyl-2,3-dihydrobenzofuran (5t) and *trans*-7-methoxy-2-(4-methoxy-2-pivaloyloxyphenyl)-3-vinyl-2,3-dihydrobenzofuran (6t)**: Reaction of 9-methoxybenzoxasilepin (**7**) (116 mg, 0.53 mmol) with 4-methoxy-2-pivaloyloxybenzaldehyde (**4c**) (149 mg, 0.63 mmol) and $BF_3{\cdot}Et_2O$ (130 μL, 1.06 mmol) in anhydrous CH_2Cl_2 (2.5 mL) followed by workup, as described in the general procedure, yielded **5t**/**6t** 9:91 with an overall yield of 57%.

*Compound **6t***: Colourless oil; R_f=0.25 (hexane/Et_2O 95:5); ^{1}H NMR (300 MHz, $CDCl_3$, 25°C, TMS): δ=7.39 (d, ^3J(H,H)=8.7 Hz, 1H; H-6′), 6.90 (dd, ^3J(H,H)=8.1, 7.2 Hz, 1H; H-5), 6.83 (d, ^3J(H,H)=7.2 Hz, 1H; H-6), 6.79 (dd, ^3J(H,H)=8.7, 2.6 Hz, 1H; H-5′), 6.74 (d, ^3J(H,H)=7.2 Hz, 1H; H-4), 6.57 (d, ^3J(H,H)=2.6 Hz, 1H; H-3′), 5.90 (dt, ^3J(H,H)=17.6, 8.5 Hz, 1H; H-1″), 5.55 (d, ^3J(H,H)=8.5 Hz, 1H; H-2), 5.15 (m, 2H; H-2″), 4.07 (t, ^3J(H,H)=8.5 Hz, 1H; H-3), 3.91 (s, 3H; OCH_3), 3.81 (s, 3H; OCH_3), 1.30 ppm (s, 9H; $C(CH_3)_3$); ^{13}C NMR (75 MHz, $CDCl_3$, 25°C, TMS): δ=176.6 (C, COO−), 160.0 (C, C-4′), 149.3 (C, C-2′), 147.6 (C, C-7a), 144.4 (C, C-7), 136.8 (CH, C-1″), 130.1 (C, C-3a), 128.5 (CH, C-6′), 124.1 (C, C-1′), 121.5 (C, C-5), 117.6 (CH_2, C-2″), 117.0 (CH, C-4), 112.2 (CH, C-5′), 111.9 (CH, C-6), 107.9 (CH, C-3′), 85.3 (CH, C-2), 56.0 (OCH_3), 55.7 (CH, C-3), 55.4 (OCH_3), 39.2 (C, $C(CH_3)_3$), 27.1 ppm (CH_3, $C(CH_3)_3$); IR (film): $\tilde{\nu}$=2963, 2934, 2837, 1753, 1617, 1587, 1489, 1458, 1282, 1110, 1032, 801 cm^{-1}; HR-EIMS: *m/z*: calcd for $C_{23}H_{26}O_5$: 382.1780 $[M]^+$; found: 382.1781.

***cis*-2-(2,4-Dipivaloyloxyphenyl)-7-methoxy-3-vinyl-2,3-dihydrobenzofuran (5u) and *trans*-2-(2,4-dipivaloyloxyphenyl)-7-methoxy-3-vinyl-2,3-dihydrobenzofuran (6u)**: Reaction of 9-methoxybenzoxasilepin (**7**) (157 mg, 0.72 mmol) with 2,4-dipivaloyloxybenzaldehyde (**4h**) (149 mg, 0.63 mmol) and $BF_3{\cdot}Et_2O$ (130 μL, 1.06 mmol) in anhydrous CH_2Cl_2 (3.5 mL) followed by workup, as described in the general procedure, yielded **5u**/**6u** 50:50 with an overall yield of 60%.

*Compound **5u***: Colourless oil; R_f=0.29 (hexane/Et_2O 95:5); ^{1}H NMR (300 MHz, $CDCl_3$, 25°C, TMS): δ=7.56 (d, ^3J(H,H)=8.1 Hz, 1H; H-6′), 6.97 (dd, ^3J(H,H)=8.1, 2.2 Hz, 1H; H-5′), 6.95 (br s, 1H; H-3′), 6.90 (t, ^3J(H,H)=7.1 Hz, 1H; H-5), 6.85* (dd, ^3J(H,H)=7.1, 1.2 Hz, 1H; H-4), 6.78* (br d, ^3J(H,H)=7.1 Hz, 1H; H-6), 5.98 (d, ^3J(H,H)=8.9 Hz, 1H; H-2), 5.35 (ddd, ^3J(H,H)=16.9, 9.9, 8.5 Hz, 1H; H-1″), 4.95 (br d, 1H; ^3J(H,H)=16.9 Hz; H-2″b), 4.95 (br d, ^3J(H,H)=10.5 Hz, 1H; H-2″a), 4.24 (dd, ^3J(H,H)=8.9, 8.5 Hz, 1H; H-3), 3.95 (s, 3H; OCH_3), 1.38 (s, 9H; $C(CH_3)_3$), 1.35 ppm (s, 9H; $C(CH_3)_3$); * may be interchanged; ^{13}C NMR (75 MHz, $CDCl_3$, 25°C, TMS): δ=176.6 (C, COO−), 175.8 (C, COO−), 150.6 (C, C-2′), 147.6 (C, C-7a), 147.4 (C, C-4), 144.6 (C, C-7), 135.4 (CH, C-1″), 129.9 (C, C-3a), 127.9 (CH, C-6′), 127.0 (C, C-1′), 121.7 (C, C-5), 118.5 (CH, C-5′), 117.9 (CH, C-4), 116.9 (CH_2, C-2″), 115.3 (CH, C-3′), 111.9 (CH, C-6), 83.0 (CH, C-2), 56.1 (OCH_3), 50.9 (CH, C-3), 39.2 (C, $C(CH_3)_3$), 39.1 (C, $C(CH_3)_3$), 27.1 ppm (CH_3, $C(CH_3)_3$); IR (film): $\tilde{\nu}$=2973, 2934, 1755, 1611, 1492, 1279, 1106, 911, 743 cm^{-1}; HR-EIMS: *m/z*: calcd for $C_{27}H_{32}O_6$: 452.2199 $[M]^+$; found: 452.2196.

*Compound **6u***: White solid; R_f=0.28 (hexane/Et_2O 95:5); ^{1}H NMR (300 MHz, $CDCl_3$, 25°C, TMS): δ=7.49 (d, ^3J(H,H)=8.5 Hz, 1H; H-6′), 6.97 (dd, ^3J(H,H)=8.5, 2.2 Hz, 1H; H-5′), 6.90 (dd, ^3J(H,H)=7.5, 7.2 Hz, 1H; H-5), 6.86 (m, 2H; H-3′,6), 6.73 (br d, ^3J(H,H)=7.2 Hz, 1H; H-4), 5.91 (ddd, ^3J(H,H)=17.9, 9.1, 8.4 Hz, 1H; H-1″), 5.61 (d, ^3J(H,H)=8.2 Hz, 1H; H-2), 5.17 (m, 2H; H-2″), 4.06 (t, ^3J(H,H)=8.4 Hz, 1H; H-3), 3.92 (s, 3H; OCH_3), 1.35 (s, 9H; $C(CH_3)_3$), 1.30 ppm (s, 9H; $C(CH_3)_3$); ^{13}C NMR (75 MHz, $CDCl_3$, 25°C, TMS): δ=176.5 (C, COO−), 175.3 (C, COO−), 151.0 (C, C-2′), 148.6 (C, C-4′), 147.5 (C, C-7a), 144.4 (C, C-7), 136.7 (CH, C-1″), 129.9 (C, C-3a), 129.4 (C, C-1′), 128.1 (CH, C-6′), 121.7 (CH, C-5), 119.2 (CH, C-5′), 117.8 (CH_2, C-2″), 117.0 (CH, C-4), 116.0 (CH, C-3′), 111.9 (CH, C-6), 85.0 (CH, C-2), 56.0 (OCH_3), 55.9 (CH, C-3), 39.2 (C, $C(CH_3)_3$), 39.1 (C, $C(CH_3)_3$), 27.0 ppm (CH_3, $C(CH_3)_3$); IR (KBr): $\tilde{\nu}$=2971, 2930, 1756, 1613, 1591, 1492, 1459, 1281,

1106, 956, 919, 756, 727 cm^{-1};HR-EIMS: *m/z*: calcd for $C_{27}H_{32}O_6$: 452.2199 $[M]^+$; found: 452.2196.

***cis*-5-Methoxy-2-(4-methoxy-2-pivaloyloxyphenyl)-3-vinyl-2,3-dihydrobenzofuran (5v) and *trans*-5-methoxy-2-(4-methoxy-2-pivaloyloxyphenyl)-3-vinyl-2,3-dihydrobenzofuran (6v)**: Reaction of 7-methoxybenzoxasilepin (**8**) (231 mg, 1.05 mmol) with 4-methoxy-2-pivaloyloxybenzaldehyde (**4c**) (322 mg, 1.36 mmol) and $BF_3{\cdot}Et_2O$ (260 μL, 2.1 mmol) in anhydrous CH_2Cl_2 (5.0 mL) followed by workup, as described in the general procedure, yielded **5v**/**6v** 20:80 with an overall yield of 60%.

*Compound **5v***: Colourless oil; R_f=0.28 (hexane/Et_2O 95:5); ^1H NMR (300 MHz, $CDCl_3$, 25°C, TMS): δ=7.38 (d, ^3J(H,H)=8.6 Hz, 1H; H-6′), 6.85 (d, ^3J(H,H)=8.6 Hz, 1H; H-7), 6.77* (dd, ^3J(H,H)=8.6, 2.5 Hz, 1H; H-6), 6.76* (dd, ^3J(H,H)=8.6, 2.8 Hz, 1H; H-5′), 6.71 (d, ^3J(H,H)=2.1 Hz, 1H; H-4), 6.64 (d, ^3J(H,H)=2.5 Hz, 1H; H-3′), 5.87 (d, ^3J(H,H)=8.9 Hz, 1H; H-2), 5.35 (ddd, ^3J(H,H)=17.1, 10.0, 8.6 Hz, 1H; H-1″), 4.97 (d, ^3J(H,H)=17.1 Hz, 1H; H-2″b), 4.93 (d, ^3J(H,H)=10.0 Hz, 1H; H-2″a), 4.17 (t, ^3J(H,H)=8.6 Hz, 1H; H-3), 3.80 (s, 3H; OCH_3), 3.78 (s, 3H; OCH_3), 1.39 ppm (s, 9H; $C(CH_3)_3$); ^{13}C NMR (75 MHz, $CDCl_3$, 25°C, TMS): δ=176.1 (C, COO−), 159.6 (C, C-4′), 154.4 (C, C-5), 153.3 (C, C-7a), 148.2 (C, C-2′), 135.7 (CH, C-1″), 129.7, (C, C-3a), 127.9 (CH, C-6′), 122.2 (C, C-1′), 116.7 (CH_2, C-2″), 113.8 (CH, C-6), 111.6[#] (CH, C-4), 111.5[#], (CH, C-5′), 109.6 (CH, C-7), 107.4 (CH, C-3′), 82.6 (CH, C-2), 55.9 (OCH_3), 55.4 (OCH_3), 51.2 (CH, C-3), 39.2 (C, $C(CH_3)_3$), 27.2 ppm (CH_3, $C(CH_3)_3$); * and [#] may be interchanged; IR (film): $\tilde{\nu}$=2927, 1753, 1486, 1210, 1113, 913, 745 cm^{-1}; HR-EIMS: *m/z*: calcd for $C_{23}H_{26}O_5$: 382.1780 $[M]^+$; found: 382.1785.

*Compound **6v***: Colourless oil; R_f=0.27 (hexane/Et_2O 95:5); ^1H NMR (300 MHz, $CDCl_3$, 25°C, TMS): δ=7.37 (d, ^3J(H,H)=8.6 Hz, 1H; H-6′), 6.81–6.69 (m, 3H; H-4, 6, 5′, 7), 6.59 (d, ^3J(H,H)=2.4 Hz, 1H; H-3′), 5.91 (ddd, ^3J(H,H)=17.3, 8.9, 8.6 Hz, 1H; H-1″), 5.45 (d, ^3J(H,H)=8.3 Hz, 1H; H-2), 5.18 (d, ^3J(H,H)=11 Hz, 1H; H-2″a), 5.17 (d, ^3J(H,H)=15.8 Hz, 1H; H-2″b), 4.04 (t, ^3J(H,H)=8.3 Hz, 1H; H-3), 3.81 (s, 3H; OCH_3), 3.78 (s, 3H; OCH_3), 1.31 ppm (s, 9H; $C(CH_3)_3$); ^{13}C NMR (75 MHz, $CDCl_3$, 25°C, TMS): δ=176.62 (C, COO−), 160.1 (C, C-4′), 154.4* (C, C-7a), 153.3* (C, C-5), 149.4 (C, C-2′), 136.7 (CH, C-1″), 130.0, (C, C-3a), 128.4 (CH, C-6′), 124.1 (C, C-1′), 117.8 (CH_2, C-2″), 113.8[#] (CH, C-4), 110.8[#] (C, C-6), 109.6[#], (CH, C-7), 112.1 (CH, C-5′), 108.1 (CH, C-3′), 85.1 (CH, C-2), 56.0 (CH, C-3), 55.5 (OCH_3), 55.4 (OCH_3), 39.1 (C, $C(CH_3)_3$), 27.1 ppm (CH_3, $C(CH_3)_3$); * and [#] may be interchanged; IR (film): $\tilde{\nu}$=2967, 1753, 1618, 1508, 1486, 1273, 1210, 1112, 1033 cm^{-1}; HR-EIMS: *m/z*: calcd for $C_{23}H_{26}O_5$: 382.1780 $[M]^+$; found: 382.1776.

***cis*-2-(2,4-Dipivaloyloxyphenyl)-5-methoxy-3-vinyl-2,3-dihydrobenzofuran (5w) and *trans*-2-(2,4-dipivaloyloxyphenyl)-5-methoxy-3-vinyl-2,3-dihydrobenzofuran (6w)**: Reaction of 7-methoxybenzoxasilepin (**8**) (168 mg, 0.76 mmol) with 2,4-dipivaloyloxybenzaldehyde (**4h**) (280 mg, 0.92 mmol) and $BF_3{\cdot}Et_2O$ (190 μL, 1.52 mmol) in anhydrous CH_2Cl_2 (3.5 mL) followed by workup, as described in the general procedure, yielded **5w**/**6w** 91:9 with an overall yield of 60%.

*Compound **5w***: Colourless oil; R_f=0.28 (hexane/Et_2O 95:5); ^1H NMR (300 MHz, $CDCl_3$, 25°C, TMS): δ=7.50 (d, ^3J(H,H)=8.1 Hz, 1H; H-6′), 6.97 (dd, ^3J(H,H)=8.1, 2.1 Hz, 1H; H-5′), 6.95 (brs, 1H; H-3′), 6.87 (d, ^3J(H,H)=8.5, 1H; H-7), 6.77 (dd, ^3J(H,H)=8.5, 2.6 Hz, 1H; H-6), 6.71 (d, ^3J(H,H)=2.6 Hz, 1H; H-4), 5.92 (d, ^3J(H,H)=8.9 Hz, 1H; H-2), 5.32 (ddd, ^3J(H,H)=18.1, 9.8, 8.5 Hz, 1H; H-1″), 4.98 (brd, ^3J(H,H)=18.1 Hz, 1H; H-2″b), 4.93 (brd, ^3J(H,H)=9.8 Hz, 1H; H-2″a), 4.22 (dd, ^3J(H,H)=8.9, 8.5 Hz, 1H; H-3), 3.78 (s, 3H; OCH_3), 1.39 (s, 9H; $C(CH_3)_3$), 1.36 ppm (s, 9H; $C(CH_3)_3$); ^{13}C NMR (75 MHz, $CDCl_3$, 25°C, TMS): δ=176.5 (C, COO−), 175.8 (C, COO−), 154.5 (C, C-5), 153.2 (C, C-7a), 150.6 (C, C-4′), 147.6 (C, C-2′), 135.4 (CH, C-1″), 129.6, (C, C-3a), 127.6 (CH, C-6′), 127.5 (C, C-1′), 118.6 (CH, C-5′), 117.0 (CH_2, C-2″), 115.4 (CH, C-3′), 114.0 (CH, C-6), 111.6 (CH, C-4), 109.7 (CH, C-7), 82.1 (CH, C-2), 56.0 (OCH_3), 51.2 (CH, C-3), 39.2 (*C*, $C(CH_3)_3$), 39.1 (*C*$(CH_3)_3$), 27.1 (CH_3, $C(CH_3)_3$), 27.1 ppm (CH_3, $C(CH_3)_3$); IR (film): $\tilde{\nu}$=2973, 2934, 2873, 1756, 1485, 1271, 1211, 1108, 1029 cm^{-1}; HR-EIMS: *m/z*: calcd for $C_{27}H_{32}O_6$: 452.2199 $[M]^+$; found: 452.2197.

*Compound **6w***: Colourless oil; R_f=0.27 (hexane/Et_2O 95:5); ^1H NMR (300 MHz, $CDCl_3$, 25°C, TMS): δ=7.47 (d, ^3J(H,H)=8.6 Hz, 1H; H-6′), 6.97 (dd, ^3J(H,H)=8.6, 2.4 Hz, 1H; H-5′), 6.86 (d, ^3J(H,H)=2.4 Hz, 1H; H-3′), 6.81 (d, ^3J(H,H)=8.6 Hz, 1H; H-7), 6.76 (dd, ^3J(H,H)=8.6, 2.7 Hz, 1H; H-6), 6.68 (d, ^3J(H,H)=2.4 Hz, 1H; H-4), 5.92 (ddd, ^3J(H,H)=16.9, 10.8, 8.6 Hz, 1H; H-1″), 5.52 (d, ^3J(H,H)=8.1 Hz, 1H; H-2), 5.19 (brd, ^3J(H,H)=10.8 Hz, 1H; H-2″a), 5.18 (brd, ^3J(H,H)=16.9 Hz, 1H; H-2″b), 4.01 (t, ^3J(H,H)=8.1 Hz, 1H; H-3), 3.78 (s, 3H; OCH_3), 1.36* (s, 9H; $COC(CH_3)_3$), 1.31* ppm (s, 9H; $COC(CH_3)_3$); ^{13}C NMR (75 MHz, $CDCl_3$, 25°C, TMS): δ=176.5* (C, *CO*$C(CH_3)_3$), 176.4* (C, *CO*$C(CH_3)_3$), 154.6 (C, C-5), 153.3 (C, C-7a), 151.0 (C, C-4′), 148.7 (C, C-2′), 136.7 (CH, C-1″), 129.6[#] (C, C-1′), 129.7[#] (C, C-3a), 128.0 (CH, C-6′), 119.1 (CH, C-5′), 117.9 (CH_2, C-2″), 116.1 (CH, C-3′), 114.0 (CH, C-6), 110.8 (CH, C-4), 109.6 (CH, C-7), 84.7 (CH, C-2), 56.0 (OCH_3), 55.6 (CH, C-3), 39.2 (C, CO*C*$(CH_3)_3$), 39.1 (CO*C*$(CH_3)_3$), 27.1 (CH_3, $COC(CH_3)_3$), 27.0 ppm (CH_3, $COC(CH_3)_3$); * and [#] may be interchanged; IR (film): $\tilde{\nu}$=2972, 2933, 2874, 1757, 1611, 1486, 1432, 1397, 1367, 1248, 1203, 1144, 1106, 1030, 806 cm^{-1}; HR-FABMS: *m/z*: calcd for $C_{27}H_{32}O_6Na$: 475.2100 $[M+Na]^+$; found: 475.2100.

***cis*-5-Methoxy-2-(5-methoxy-2-pivaloyloxyphenyl)-3-vinyl-2,3-dihydrobenzofuran (5x)**: Reaction of 7-methoxybenzoxasilepin (**8**) (243 mg, 1.1 mmol) with 5-methoxy-2-pivaloyloxybenzaldehyde (**4i**) (285 mg, 1.21 mmol) and $BF_3{\cdot}Et_2O$ (280 μL, 2.2 mmol) in anhydrous CH_2Cl_2 (5.5 mL) followed by workup, as described in the general procedure, above yielded **5x** (262 mg, 0.68 mmol, 62%). Colourless oil; R_f=0.28 (hexane/Et_2O 95:5); ^1H NMR (300 MHz, $CDCl_3$, 25°C, TMS): δ=7.06 (d, ^3J(H,H)=3.0 Hz, 1H; H-6′), 7.02 (d, ^3J(H,H)=8.9 Hz, 1H; H-3′), 6.87 (d, ^3J(H,H)=8.6 Hz, 1H; H-7), 6.85 (dd, ^3J(H,H)=8.9, 3.0 Hz, 1H; H-4′), 6.78 (dd, ^3J(H,H)=8.6, 2.6 Hz, 1H; H-6), 6.73 (d, ^3J(H,H)=2.6 Hz, 1H; H-4), 5.89 (d, ^3J(H,H)=8.8 Hz, 1H; H-2), 5.37 (ddd, ^3J(H,H)=17.7, 9.2, 7.8 Hz, 1H; H-1″), 5.00 (brd, ^3J(H,H)=17.7 Hz, 1H; H-2″b), 4.93 (dd, ^3J(H,H)=9.2, 1.7 Hz, 1H; H-2″a), 4.22 (dd, ^3J(H,H)=8.8, 7.8 Hz, 1H; H-3), 3.79 (s, 6H; OCH_3), 1.40 ppm (s, 9H; $OCOC(CH_3)_3$); ^{13}C NMR (75 MHz, $CDCl_3$, 25°C, TMS): δ=176.6 (C, O*CO*$C(CH_3)_3$), 157.0 (C, C-5′), 154.5 (C, C-5), 153.2 (C, C-7a), 141.0 (C, C-2′), 135.5 (CH, C-1″), 131.2 (C, C-1′), 129.7 (C, C-3a), 122.6 (CH, C-3′), 116.7 (CH_2, C-2″), 114.0 (CH, C-6), 113.6 (CH, C-4′), 112.1 (CH, C-6′), 111.6 (CH, C-4), 109.7 (CH, C-7), 82.8 (CH, C-2), 56.0* (CH_3, OCH_3), 55.5* (CH_3, OCH_3), 51.1 (CH, C-3), 39.1 (C, OCO*C*$(CH_3)_3$), 27.2 ppm (CH_3, $OCOC(CH_3)_3$); * may be interchanged; IR (film): $\tilde{\nu}$=3078, 2972, 2936, 2910, 2834, 1750, 1607, 1487, 1429, 1364, 1273, 1210, 1118, 1034, 982, 800 cm^{-1}; HR-FABMS: *m/z*: calcd for $C_{23}H_{26}O_5Na$: 405.1678 $[M+Na]^+$; found: 405.1676.

(*Z*)-2-(3-Fluorodimethylsilyl-1-propenyl)phenol (9): To a solution of 2,2-dimethyl-2,3-dihydrobenzo[*f*][1,2]oxasilepin (**3**) (50 mg, 0.26 mmol) in methanol (0.5 mL) was added $BF_3{\cdot}Et_2O$ (66 μL, 0.52 mmol). The mixture was stirred at room temperature for 5 min and then diluted with CH_2Cl_2 (10 mL) and washed with brine (5 mL). The organic phase was dried over $MgSO_4$ and evaporated under vacuo to give compound **9** (43 mg, 0.24 mmol, 90% yield). Colourless oil; ^1H NMR (300 MHz, $CDCl_3$, 25°C, TMS): δ=7.20 (dd, ^3J(H,H)=8.0, 7.4 Hz, 1H; H-5), 7.12 (d, ^3J(H,H)=7.5 Hz, 1H; H-3), 6.92 (m, 2H; H-4, H-6), 6.38 (d, ^3J(H,H)=11.4 Hz, 1H; H-1′), 6.02 (dt, ^3J(H,H)=11.1, 8.7 Hz, 1H; H-2′), 1.79 (dd, ^3J(H,H)=7.8, ^3J(H,F)=5.8 Hz, 2H; H-3′); 0.23 (d, ^3J(H,F)=7.4 Hz, 6H; H-4′); ^{19}F NMR (289 MHz, $CDCl_3$, 25°C): −161.74 ppm (hept t, ^3J(F,H)=7.4, ^3J(F,H)=5.8 Hz, 1F; $SiMe_2F$); ^{13}C NMR (75 MHz, $CDCl_3$, 25°C, TMS): δ=152.4 (C, C-1), 130.5* (CH, C-3), 129.6* (CH, C-5), 128.6 (CH, C-2′), 123.3 (C, C-2), 122.8 (CH, C-1′), 120.3 (CH, C-4), 115.1 (CH, C-6), 20.0 (CH_2, d, ^2J(C,F)=13.1 Hz, C-3′), −1.5 ppm (CH_3, d, ^2J(C,F)=14.9 Hz, C-4′); * may be interchanged; IR (film): $\tilde{\nu}$=3567, 3528, 3423, 2958, 2926, 2870, 1601, 1579, 1484, 1449, 1381, 1337, 1256, 1212, 1158, 1090, 874, 843, 798 cm^{-1}; HR-EIMS: *m/z*: calcd for $C_{11}H_{15}OsiF$: 210.0876 $[M+Na]^+$; found: 210.0873; mixture **3**/**II**: ^1H NMR (300 MHz, $CDCl_3$, 25°C, TMS); common signals: δ=7.19 (m, 2H), 7.13 (m, 2H), 6.95 (m, 4H), 6.39 ppm (d, 2H, *J*=11.4 Hz; H-1′); signals due to **3**: δ=6.10 (dt, ^3J(H,H)=10.8, ^3J(H,H)=7.5 Hz, 1H; H-4), 1.58 (d, ^3J(H,H)=7.4 Hz, 2H; H-3), 0.33 ppm ($SiMe_2$; 6H); signals due to **II**: δ=6.02 (dt, ^3J(H,H)=11.1, 8.7 Hz, 1H; H-2′), 1.78 (dd, ^3J(H,H)=7.8, ^3J(H,F)=5.8 Hz, 2H; H-3′); 0.23 ppm (d, ^3J(H,F)=7.4 Hz, 6H; H-4′).

General procedure used to obtained data in Table 4: $BF_3{\cdot}Et_2O$ (0.32 mmol) was added to a solution of benzoxasilepin (30 mg, 0.16 mmol) and the aldehyde (0.16 mmol) in $CDCl_3$ (0.5 mL) in a NMR tube. The mixture was heated to 40 °C in an oil bath and, after 6 h, the ^{1}H NMR spectrum was acquired. The ratio *cis*/*trans* was determined by measuring the area of H-2 and H-3 signals for both diasteromers.

General procedure used to obtained data of Figure 4: $BF_3{\cdot}Et_2O$ (1.6 mmol) was added to a solution of benzoxasilepin (30 mg, 0.16 mmol) in [D_7]DMF (0.5 mL) in a NMR tube. The mixture was heated to the following temperatures and the ^{1}H NMR spectrum was acquired. The ratio **II/3** (K) was determined by measuring the area of $Si(CH_3)_3$ signals for each compound. K (T [K]): 10.0 (258), 5.5 (278), 3.5 (298), 2.6 (308), 2.3 (323), 1.6 (343).

X-ray crystallography of 5l and 6b

Crystal data for ***5l***: $C_{21}H_{16}O_3$, $M=316.34$, orthorhombic, space group *Pbca*, $a=7.3789(6)$, $b=19.3297(16)$, $c=25.302(2)$ Å, $\alpha=90$, $\beta=90$, $\gamma=90°$; $V=3608.8(5)$ Å^3, $T=273$ K, $Z=8$, $\mu(Mo_{K\alpha})=0.077$ mm^{-1}. A total of 16407 reflections were collected, 2579 unique reflections ($R_{int}=0.0430$) which were used in all calculations. The final wR (F^2) was 0.2107 (all data).

Crystal data for ***6b***: $C_{17}H_{16}O_2$, $M=252.30$, orthorhombic, space group $P2(1)2(1)2(1)$, $a=6.0770(14)$, $b=7.5441(16)$, $c=29.082(7)$ Å, $\alpha=90$, $\beta=90$, $\gamma=90°$, $V=1333.3(5)$ Å^3, $T=273$ K, $Z=4$, $\mu(Mo_{K\alpha})=0.081$ mm^{-1}. A total of 6113 reflections were collected, 1909 unique reflections ($R_{int}=0.0838$) which were used in all calculations. The final wR (F^2) was 0.1397 (all data).

CCDC-613456 and -613457 contain the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

Acknowledgements

We wish to acknowledge the Spanish Ministerio de Educación y Ciencia for financial support (Projects PB98-1006 and BQU2002-03254) and for scholarships to L. Jiménez-González and S. García Muñoz.

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[39] ^{1}H NMR spectra recorded in EtOH by using [D_6]DMSO as the external standard.
[40] Selected bond lengths [Å] and bond angles [°]: O1−C9 1.462(3), C7−C9 1.561(4), C7−C12 1.490(4), C12−C19 1.293(5), C4−C9 1.513(4), C7−H7 0.980, C9−H9 0.980; C6-O1-C9 107.4(2), C7-C12-C19 124.1(3), O1-C9-C7 105.6(2), O1-C9-C4 109.8(2), C5-C7-C9 101.2(2), H7-C7-C9-H9 −22.2.
[41] Selected bond lengths [Å] and bond angles [°]: O1−C8 1.463(5), C7−C8 1.557(5), C8−C9 1.502(5), C7−C15 1.485(6), C15−C16 1.312(6), C8−H8 0.980, C7−H7 0.980, C6−C7 1.532(6), C1−O1 1.375(5); C23-C22-H22 106.3, C1-O1-C8 106.4(3), C7-C15-C16 121.6(4), O1-C8-C9 109.0(3), C6-C7-C8 98.4(3), C15-C7-C6 114.5(4), C1-C6-C2 108.9(4), H7-C7-C8-H8 157.4.
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Received: July 17, 2006
Published online: September 29, 2006

